



# PHOTOGRAPHIC SCIENCE and TECHNIQUE

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TECHNICAL QUARTERLY  
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SOCIETY OF AMERICA



## AUTOMATIC-RECORDING TOTALIZING DENSITOMETER

A COMPONENT DISTRIBUTION CURVE and an accompanying saw-tooth totalizing curve are produced simultaneously in the new Spincro Analytrol as a variable density strip—such as a paper electrophoresis pattern—is automatically drawn through the scanning mechanism. Alternatively, the automatic totalizing curve can be produced from any existing distribution curve by manual following of the original curve.

Auxiliary mechanisms are available from the manufacturer, Specialized Instruments Corporation, of Belmont, California. These permit operation with ultraviolet rather than visible light and adapt for the colorimetric recording of stationary or moving fluids in tubes. Accessories are under development for the production of similar traces derived from strips containing patterns with various concentrations of radioactive materials.

Functionally, the Analytrol is a null or unbalanced device utilizing a system of two barrier-layer photocells illuminated from a single light source. The material to be scanned is passed before one of the cells, causing an output current drop and unbalancing a bridge circuit. The unbalanced signal is amplified and used to drive a motor which interposes a light-shielding cam in front of the other photocell until balance is restored. This same mechanism drives the curve-drawing and integration pens.

Because of this light-shielding cam principle, various mathematical functions can be introduced to accommodate for differences in response between the optical density and the actual concentration of material. For example, in paper electrophoresis analysis, a special cam is available to coordinate with a bromphenol blue dyeing technique. This can be changed to accommodate the use of other dyes.

Other features of the photocell-balance principle are that line voltage variations and aging of the light source or amplifier components are cancelled out and uniform accuracy is maintained under varying conditions.

Maximum width of the curve-drawing paper-feed is 12 inches. Maximum width of the scanned strip is 2 inches. Maximum height of the finished distribution curve is 6 1/2 inches. The integration curve is drawn in such a way that every tenth pip in the sawtooth configuration is extended for convenience in counting and tabulation. The complete instrument has dimensions of 16 3/8 by 15 7/8 by 10 1/2 inches; weighs a total of 50 pounds. Operation is from a standard 115-v 50/60 cps source drawing 125 watts.

## STRANGE SPOTS

THE SERVICE DEPARTMENTS maintained by photographic manufacturers to aid their customers in the solving of photographic problems sometimes are confronted themselves with problems that are mighty difficult to solve. The following letter from the Eastman Kodak Company Sales Service Division testifies to one such instance.

"We made a study of the ghost images on your 4 X 5 negatives. In general, the outline of these spots is similar to the shape of your lens diaphragm. While such images can be caused by the presence of bright lights either in the field of view or just outside the field of view, we are inclined to think they are caused by small airborne objects close to the camera and brightly illuminated by the flash bulb.

"Examination of the spots shows that the objects were moving in random directions. This would indicate that the

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PHOTOGRAPHIC SCIENCE AND TECHNIQUE is dedicated to the publication of scientific and technical papers dealing with the theory and practice of photography. Its aim is to encourage the publication of authoritative articles describing original research, techniques, and the engineering aspects of new equipment in all fields of photography. It is intended to interest and inform the advanced amateurs, the professionals, the technologists, and the scientists who study or apply photographic processes.

Established in 1950, Photographic Science and Technique is prepared under the editorial management and control of the Technical Division of the Society. The first four volumes were

counted as Section B of the PSA Journal and numbered 168 to 198 inclusively. As a separate publication, Series II, Volume 1, Number 1 started in the first quarter of 1954.

Members of the Photographic Society are entitled to receive both the monthly PSA Journal and this quarterly technical publication. Non-member subscriptions are available only to libraries, schools, and Government units at \$5.00 a year (\$9.00 for two years) for both publications together. Separate subscriptions are not available. Single copies, including back issues when available, at Society Headquarters in Philadelphia, \$1.00 a copy. No extra charge for overseas mailing.

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objects were insects—possibly mosquitoes or moths—attracted by the headlights at the scene of the accident.

"If, for example, the insect were within a few feet of your camera and within its field of view, and the camera were focused for a much greater distance, the intensely illuminated insect would record not in the shape of an insect but it would be so badly out of focus that it would form an image of the camera lens diaphragm. If the insect were farther away, the spot would be fainter and smaller in size. A very small insect close to the camera would record as a large but faint spot."

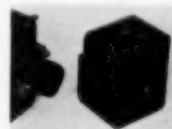


The strange spots that fill the sky in the upper photograph are images of the lens diaphragm, fairly sharply defined, caused by flash light reflections from a swarm of small insects close to the camera, therefore out of focus. In the center picture the bright central spot is caused by a large insect close to the camera. Two spots higher up indicate by their trails the directions in which the insects were moving. The bottom picture shows a clearly defined image of the lens diaphragm caused by an insect. Pictures by Jack Lord, Orlando, Fla.

## GUN CAMERA ATTACHMENT

U. S. NAVY SCIENTISTS have put the pull of gravity and centrifugal force to work to photograph aircraft rocket hits. They devised an attachment for a 16mm camera that automatically keeps it focussed on the target to record rocket hits or misses after the pilot pulls the plane out of its firing dive.

The inventors are John S. Attinello and Charles H. Harry. Their device tilts a system of mirrors downward in proportion to the vertical pull. The Navy calls it ADOG—Automatic Depressor of the Optical Axis for Gun Cameras.



## REPORT ON A CONFERENCE ON THE SCIENTIFIC AND TECHNICAL APPLICATIONS OF PHOTOGRAPHY\*

ANOTHER ONE DAY CONFERENCE in the series organized by the Scientific & Technical Group of the Royal Photographic Society was held on October 2, 1954 in the Stephenson Building, King's College, Durham University, Newcastle-upon-Tyne. About 80 people attended, many of them representing local industries. The programme, which was devoted to the scientific and technical applications of photography, included papers by members of the University Staff as well as by outside speakers.

The first paper was given by Messrs. A. F. B. Young and D. Legg, on the application of photographic techniques in industrial electrical research. A description was given of a high-speed rotating block compensator camera developed for research in circuit breaking and similar problems.

A paper by Mr. D. P. Blight (Department of Agricultural Engineering) was devoted to the determination of the emergent velocity of dust particles in the application of insecticidal dusts. The particles are photographed as they emerge from the jet orifice by means of collimated illumination against a black background.

Mr. E. H. Boulton and Dr. H. R. Thirsk (Dept. of Physical Chemistry) described the application of electron-optical techniques in electro-chemistry. In the last paper of the morning session, Mr. R. J. Hercock reviewed the nature and formation of the latent image and the influence of such factors as image spread in the emulsion, contrast and graininess on resolving power and the appearance of the final picture.

The first paper of the afternoon session by Messrs. R. L. Townsin and W. Robson (Dept. of Naval Architecture), dealt with photographing cavitation on model propellers. Mr. C. S. W. Brice was concerned with the use of photography in mining safety research. Dr. Stadler (Dept. of Physical Chemistry) spoke on the use of the diffraction spectroscopy as a rapid method for the interpretation of X-ray diffraction patterns.

Dr. G. I. P. Levenson gave a review of progress in the field of the photographic development process, covering the period 1948 to 1953. The speaker dealt with work on the theory and kinetics of development and the phenomenon of super-additivity. The significance of redox potential in a developer system was referred to. Interest has been revived recently in

\* Contributed by H. G. Suggate, Hon. Secretary, on behalf of the Scientific and Technical Group of The Royal Photographic Society of Great Britain.

such topics as timing and physical development, in single solution development and fixation and in very rapid processing. The special problems in the processing of the very thick emulsions used in nuclear research were also mentioned. Some of the many compounds claimed to have useful effects in developers were described.

The last paper in the Conference was given by Mr. C. J. Duncan (Dept. of Photography, the Medical School) who re-

viewed the organization and control of a service department of photography in a University, as exemplified by his own Department. Parties were then conducted to some departments of King's College to inspect items of interest. These included the cavitation tunnel in the Dept. of Naval Architecture, the electron microscope and diffraction spectroscopy in the Dept. of Physical Chemistry, and the equipment of the Dept. of Photography in the Medical School.

## BOOKS RECEIVED

**STEREO REALIST MANUAL.** Willard D. Morgan, Henry M. Lester, and fourteen contributors. Morgan & Lester, Publishers, New York, from the Fountain Press, London, 394 pages, \$6.00.

Despite its commercial title this is a book to please anyone who is interested in stereo photography as an art, regardless of the equipment that he uses. It is a manual on practical stereo photography but covers theory in an understandable manner and some history as well.

The book is illustrated in a unique manner with both black-white and color pictures presented in stereo pairs. These can be examined by the reader in normal fashion. They can also be examined for third dimension effect, with care and imagination on the part of the reader, by making use of a plastic stereo viewer found in a pocket inside the back cover.

This lorgnette style viewer, developed by the American Optical Company, gives a fairly satisfactory stereo image for a limited number of viewings. Distances from the eye of the viewer to the lorgnette and from the latter to the printed page are critical. So is the exact orientation of the pictures. The close tolerances imposed by the viewing device make extensive viewing both time-consuming and tiring. The innovation nevertheless is a useful adjunct to a book on stereo photography and, by its novelty alone, likely to prove fascinating as well as instructive to the average reader.

The fifteen chapters have been compiled by the publishers from various sources. From the Introduction, written by avid 3-D enthusiast Harold Lloyd of Hollywood fame, to the final chapter on historical aspects, by Beaumont Newhall, the book covers the field in a remarkably thorough manner.

The first three chapters deal with the fundamentals of picture taking, the restrictions of 3-D, the mechanics of the camera advertised by the book, the characteristics of the films available for use in such cameras.

Reversal-type color films available for use in 35mm stereo cameras are discussed by John S. Carroll in terms suitable for understanding by advanced amateur photographers. The technical man may find this chapter disappointing and it contains two inconsistencies that will offend the well-informed photographer. One is the incorrect reference to "ASA Exposure Index" for color films of the reversal type. The other is the listing of Weston numbers as if they were significantly different from Exposure Indexes published by the film manufacturers for their respective products.

Helpful recommendations for the beginner as well as the more advanced worker are given by Dorothy S. Gelatt in the chapter titled "Lighting, Exposure, and Color in Stereo." Outdoor and indoor-exposures are discussed at length with instructions

for the use of exposure meters for either incident or reflected light readings. Warnings are also given on the limitations of exposure meters which so often lead the neophyte astray.

Film technicians may be startled by the remarkable assertion in this chapter: "the range of brightness that most color films can record is about 4:1." This may be a conscious distortion of the facts intended to impress the amateur with the need to choose and light his subjects properly for color photography. Knowledgeable photographers, of course, are aware that subject reflectance ratios of 6:1 or 8:1 can be reproduced on currently available materials for color photography, depending on the lighting arrangement. If lighting contrast is 2:1, the 8:1 subject reflectance ratio can be reproduced, giving a total contrast of 16:1. Almost all color photographers, using stereo cameras or conventional equipment, would be consistently disappointed if the reversal color films did not reproduce subject contrasts far above 4:1 as reported by Dorothy Gelatt.

Dick McGraw gives his personal approach to the subjects of technique and composition. This treatment is interesting and appropriate to an area in which there is always an "open season" and plenty of room for differences of opinion. Pseudoscopia is obtained by looking at the right camera image with the left eye and the left camera image with the right eye, and its mention may help some beginners to diagnose trouble of this type in their mismatched pictures.

A chapter on "Slide Mounting and Projection Equipment" by Jim Calder gives excellent instructions on mounting slides as well as the operation of the projector advertised by the book.

Robert L. McIntyre adds some technical information on the design and use of the hand viewer in the chapter on "Viewing and Projection." Adequate emphasis is placed on the problem of mounting stereo slides for projection. The realization seems to be growing that the very close tolerances for vertical mounting of stereo slides demanded for comfortable 3-D projection stands as the most serious problem in stereo techniques. Slight variations in lateral placement of the superimposed projected images can be tolerated but very slight vertical displacement causes eyestrain in the audience.

The commercial applications of stereo are broken up into three sections which include "Portrait and Fashion" by John Meredith, "Traveling With a Stereo Camera" by Julien Bryan, and "Stereo in Business, Science, and Education" by Marvin L. Rand. Ways are described in which salesmen are increasing their sales efficiency by starting out with a stereo viewer and a group of slides illustrating their products instead of the usual catalogs and sales kits.

Any beginner who has double exposed a picture has found out that he can get some very weird spacial effects by super-



imposing two or more exposures on the same picture frame. Detailed instructions for making these freak exposures in 3-D are given by Tommy Thomas in the chapter on "Sterecolusions." "Underwater Stereo" is discussed by Harry Peterson.

Binocular microscopy has been in use for many years and the use of photography for recording it is nothing new. The adaptation of the Stereo-Realist camera for the purpose is discussed by Henry M. Lester and Oscar W. Richards.

Stereo prints for viewing in the historic parlor stereoscopic viewer are as old as modern photography dating back nearly to Daguerre and Talbot in 1839. However the preparation of stereograms for reflected light viewing may have become a lost art. Instruction for handling black and white negatives and printing and mounting prints are covered in a chapter by John S. Carroll. For the avid enthusiast who is restricted in his operation by the low exposure index (10) of color reversal films there is available Kodak Direct Positive Film with exposure index of 64. With either flash or available light, this allows him to reduce his camera aperture  $2\frac{1}{2}$  full stops to obtain very much greater depth of focus or to use higher shutter speeds and stop motion. The film requires home processing through a reversal procedure and produces 35mm stereo pairs in black and white which may be mounted with the same technique used for reversal color films.

Stereoscopy grew with modern photography and became so popular that by 1880 it had invaded the well-equipped parlor all across the country with scenes of the seven wonders of the world and "Gay Paree." This evolution is ably covered in the last section, "Looking Back at Stereo" by Beaumont Newhall, curator of the Eastman Museum of Photography. An historical biography is included.

The "Stereo Realist Manual" is recommended for the beginner, the advanced amateur, and professional in stereo. Many of the chapters as well as tables on film exposure indexes and flash exposure data will also be of interest to all color enthusiasts. The authors have kept the discussion at an amateur level and wisely left out the mathematical and theoretical ramifications. It is truly a "How To Do It" manual. The book is profusely illustrated, mostly with black and white stereo pairs and has two sections with stereo prints in color.

H. C. CARLTON

INTRODUCTION TO 3-D, by H. Dewhurst, The MacMillan Company, New York, N.Y. 167 pages, \$4.50

Among professionals, amateurs and laymen it has become almost a matter of fashion to be up-to-date, at least superficially, on what is called "3-D." And yet, how frequently is one confronted with writing that shows a lack of basic knowledge, with vague phrases hardly reaching beyond the level of the functions of binocular vision. The reason may be that it all looks so simple, and so similar to the stereoscope which, two generations ago, was regarded as scarcely dispensable in a Victorian home. Also it is good to be aware of the fact that, some 2000 years ago, Euclid was cognizant of the crucial bearing that parallax had on the perception of depth in vision.

In writing this book the author has filled a gap which became increasingly noticeable as progress in "3-D" was made in recent years. If this book, as its title indicates, is intended to be only an "Introduction to 3-D," then the title can be interpreted in its best sense. The author gradually builds up in a thorough manner the foundation upon which present-

day "3-D" rests. The first chapter describes the factors of stereoscopic vision, already at this introductory stage of the book using with good advantage the analogy between the human eyes and two cameras.

In the second chapter on the geometrical requirements of stereoscopic representation, attention is drawn to the fundamental deficiencies attendant upon the artifice of a change in the spacing of camera lenses and its consequences on the sense of depth conveyed to the viewer in subsequent projection.

Parallax, perspective and convergence are explained clearly in their meaning and relative importance in stereoscopic representation. In Chapter III, the author is right to intersperse the discussion with a more quantitative treatment on how the requirements which come into play in viewing the reconstructed scene on the stereo screen can be met by basic projection methods. It is somewhat surprising and yet conceivable to see that among the inescapable geometrical conditions, which govern the satisfactory projection, some kind of psychophysics plays an important part also, "for nothing can be more natural than the illusion that the screen is a window through which we are looking" (p. 42).

In Chapter IV the viewing aids are discussed which can discriminate, as between the left and right viewing eyes, the two disparate images. There are mainly two systems which embody their own particular "eye selector" mechanisms: The roving eye system, which includes the Russian approach to stereoscopy and the better known—and nowadays preferably applied—fixed-eye system including the anaglyph, the shutter-occluding, the polarizing and the optical systems (the latter requiring the separate presentation side-by-side on the screen of the left- and right-eye images).

The following two chapters deal with the various projection methods and systems, including those which are still in an experimental stage. The reasons why today's practical systems are all of the fixed-stance two-picture type, and why most systems use Polaroid as the preferred viewing aid, are clearly explained.

Here a few words of criticisms might help the reader of later editions: It is somewhat astonishing to see mostly cameras described under the chapter heading "Projection Systems." True, a camera is a projection system, but clearer distinction between taking and reproducing systems would be advantageous. Further, the inclusion of a diagram on p. 83 would help in explaining the Dudley Beam-Splitting Anaglyph System. On page 123 a color correction filter of the kind mentioned is an orange, not a yellow filter, and the heat-dissipating (better, heat-absorbing) filter should be colorless.

Finally, the distinction between "true 3-D" and "3-D" is not a happy one (page 131). If depth impressions are conveyed to the viewer, then this is "3-D." It has not yet been established that the wide screen methods, due to the addition of peripheral vision, can claim depth impressions. The wide screen has mainly gained ground on the fact that no spectacles are required for viewing. However, it does not replace "true 3-D," i.e. binocular stereoscopic vision. There is, fortunately, no reason why a marriage of the two modes should not be within measurable sight.

In a last chapter an outlook of the possible application of 3-D techniques to stereo-television is given. Here, as in the motion-picture field, dispensing with glasses in viewing is not in sight.

A list of 33 references of the most relevant publications conclude the well-written and well-produced book. It is to be warmly welcomed and recommended as offering an excellent insight into 3-D.

H. NITKA

# FLAME GROWTH AS PORTRAYED BY CINE PHOTOGRAPHY

E. L. Gayhart, H. L. Olsen, and R. B. Edmonson\*

## ABSTRACT

Research into the incipient phase of flame propagation is currently in progress at the Applied Physics Laboratory, Johns Hopkins University. Certain aspects of the behavior and growth of spark-ignited flames are observed and recorded by photography.

The present paper describes the photographic and other experimental techniques required. There are also presented several illustrative photographic sequences which demonstrate the use of the technique and illustrate the utility of the method in carrying out flame research.

**I**N A RESEARCH INTO the incipient phases of flame propagation, certain aspects of the behavior and growth of spark-ignited flames are observed and recorded by photography. The flames are ignited in a stream of combustible gas flowing at a velocity so high that such flames do not stabilize on the burner, but are swept away into the exhaust hood. The gas stream passes through the optical path of a schlieren system which renders the flames visible, either for direct observation or for photographic record. The magnification ratio for the optical system is known, thus making it possible to analyze the development of the combustion on a quantitative basis.

The complete apparatus for a systematic study includes (1) a gas system, including a burner and an adjustable gas supply, (2) an ignition system for initiating the flames that are under study, (3) an optical system, including illumination and camera, and (4) a device for adjusting the time interval between the ignition of the flame and the flashing of the illumination to record the state of the flame at that instant.

## Components of the Apparatus

These several components are briefly described as follows. Commercial propane gas is passed through suitable reducing valves and a metering device to a mixing chamber and thence to the burner, which is a carefully formed nozzle producing a jet with a flat velocity profile. Compressed air, also through reducing valves and a similar metering device, is supplied to the same mixing chamber. The mixing ratio can be adjusted readily to any desired value.

The flames are ignited in the jet by a condenser discharge across a spark gap whose electrodes are adjustable as to gap width and height above the nozzle. The discharge is triggered by changing the grid bias of a thyatron in series with the condenser and spark gap. By use of the voltage adjustment for the power supply and by selection of the condenser capacity, the electrical energy available for the spark gap can be varied over a wide range.

\* Applied Physics Laboratory, Johns Hopkins University, Silver Spring, Maryland. Presented at the Symposium on Engineering Applications of Photography preceding the PSA National Convention in Chicago, Illinois, 5 October, 1954. Received 6 October, 1954.

Work supported by Bureau of Ordnance, U. S. Navy NOrd Contract 7386.

The optical system is best described by reference to the components in the sequence of passage of the light. By moving a reflecting prism to the appropriate position one may select as the primary illuminant either a high-intensity, short-duration spark gap or a ribbon-filament incandescent lamp. A condensing lens forms an image of the illuminant on a square aperture formed by two adjustable slits placed at right angles to each other. This square opening of adjustable size then becomes the effective light source which is placed at the principal focus of the first schlieren objective. Next in the train stands the gas nozzle, with axis vertical, and nozzle at a suitable height relative to the collimated beam. Following the burner nozzle the second schlieren objective is positioned on the optical axis at its own focal length from the burner. Beyond this lens, the beam converges to form an image of the slit. At this focal point there is located a schlieren stop in the form of a small opaque square placed on the lens surface at the center of the camera objective. The micrometer adjustments of the source slit make it possible to bring the image to the exact size of the square which blocks passage of light beyond the stop. Under the condition described, namely, with the nozzle at the principal focus of the second lens, and with a bellows extension for infinity focus, the film plane will be correctly conjugate for the transverse plane through the nozzle. The magnification ratio will be the ratio of focal lengths of the camera objective (approximately 27 in.) and second schlieren objective (8 1/2 in.).

When the optical system is correctly adjusted no light from the illuminant normally appears on the camera screen. However, any local change in the refractive index of the region between the lenses will result in a partial displacement of the slit image with consequent passage of light beyond the stop and entry into the camera. The region where the deviation originates will appear upon the camera screen as a bright area. In general, there will be formed on the screen a pattern which can be thought of as an image of the disturbance. For example, if a burning candle is placed in the collimated beam, although the flame will be imaged on the screen by its own luminosity, it will also appear to be surrounded by and to have streaming upward from it, the convection current of heated gas that is set in motion by the flame. This convection current is made vis-

ible by the light that passes through the slit in front of the first lens of the system. The use of the square aperture and square stop in lieu of the customary slit and knife edge results in a radial symmetry in the schlieren pattern which will be referred to again later.

### The Timing Device

The fourth component of the system, the timing device, is an electronic circuit developed for the purpose of this research and designated as a varitimer. The sequence of operation is simple. The ignition gap is fired and initiates a kernel of flame. The electrical radiation from the ignition gap starts a pulse through the varitimer, from which an output pulse emerges after the preset delay, and fires the illuminating spark to record the flame at an age equal to the delay.

The photographic records obtained with the system are of good contrast and good definition. Successive negatives made under the same conditions show that the phenomena involved in these investigations repeat so closely as to make indistinguishable pictures. One method of analysis of such data can be given as an example of the use of such photographs. In this method dimensions are measured of flames recorded on negatives at progressively increasing delays. From the magnification ratio and the obvious flame geometry, computations are made of the volumes of the gas involved in the combustion. From such volumes and corresponding times, the time rate of increase of volume can be derived, and thence, the burning velocity of the gas mixture.

Photographs of such a series of exposures are shown in Figure one, where there are represented flame kernels made at delay times progressing from 5 to 1000 microseconds. The progressive increase in size of the incipient flames is at once apparent, as is also the effect of the flowing gas stream in moving the kernel relative to the electrodes. In the first three views, the shock wave can be observed, expanding with the speed of sound. The impulsive effect of the spark discharge is to set up a vortex motion in the gas. Note that this vortex, which has an appearance similar to a smoke ring, can be recognized in these photographs with its edge to the viewer. The quantitative analysis of the flames shown in Figure

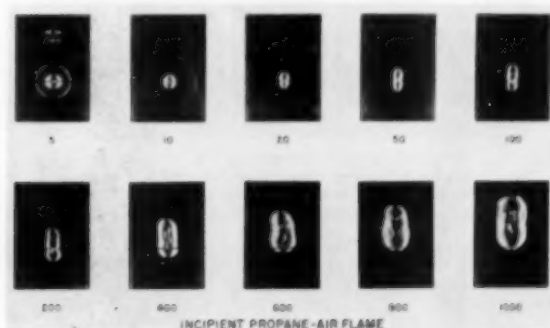


Fig. 1. Schlieren photographs of the propagation of flame from an electric spark in a vertical gas stream. Delay from ignition given in microseconds. Condenser energy 50 millijoules. Equivalence ratio 1.03.

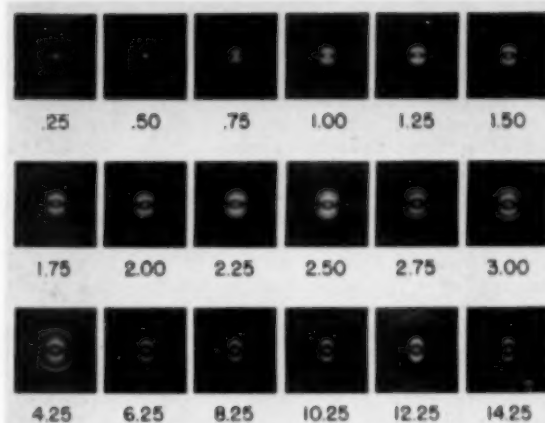


Fig. 2. Schlieren photographs of disturbances induced in still air by a condenser spark.  $1/2 \text{ cv}^2 = 250$  millijoules. Delay in time given in microseconds. Electrode shank diameter 0.025 inch.

one developed the unexpected fact that during the very early stage of flame propagation the flame velocity and temperature are considerably less than their steady state values.

Figure two demonstrates the capabilities of the apparatus for a high degree of time resolution. The details included in the first fourteen exposures of Figure two represent the entire delay of the first picture of Figure one. The increment of delay between each pair of exposures is 0.25 microsecond. If these pictures had been made by a high speed motion picture camera to record the same successive stages of development of a single flame kernel, a frame speed of four million frames per second would have been required to portray the progression in the same detail. However, it must be emphasized that each picture in Figure two is a photograph of an independent kernel. Since these pictures are made by the open-flash technique, the ignition spark which is recorded by its own light appears between the electrode tips in all the pictures. These pictures are therefore double exposures with the schlieren exposure made after the delay.

This sequence was made in air rather than combustible gas. The behavior, however, is qualitatively similar. Within the time shown here, the entire development and change in the kernel is the result of the very complicated conversion of energy that occurs in the spark path and surrounding gas. In these pictures all details except the trace of the igniting spark have been registered by light from the illuminant for the schlieren system and are to be attributed only to changes in the refractive index of the gas about the spark gap.

To examine the pictures closely note first the radial symmetry previously mentioned. The first two pictures show a faint glow or halo about the electrode tips. In the third, the glow has intensified. The fourth, at one microsecond, is similar in size, but the contrast is increased and a dark region starts in the interior. Such description applies equally to the fifth and sixth. In the sixth picture the inner kernel takes on an oval shape with longer axis in line with the electrodes. In the seventh

picture, a glow or shell appears outside a white border. This shell, which is more apparent at two microseconds continues to grow in the next two pictures although changes within the inner oval kernel are less pronounced. The shell, of which the first evidence definitely appears at 1.75 microsecond, is the shock wave set up in the air by the sudden formation of the kernel.

When the radii of the successive positions of the shock wave are plotted as a graph against corresponding times, the slope of the resulting curve represents the velocity of the expansion of the wave. This slope, originally steep, flattens to a steady value, which is the speed of sound in air. The original slope of the supersonic portion of the curve is a measure of the initial velocity of the shock wave, from which the Mach number can be determined. From the Mach number an estimate can be made of the pressure originally developed in the kernel.

### Simulated Motion Pictures

The full import of a group of pictures such as Figure two is not obvious from viewing the detached pictures. The complete development of ignition from the first appearance of a spark across the gap up to the full establishment of a flame is a complicated metamorphosis. The easily adjustable precision timing and the closely repetitive nature of the spark kernels make a condition favorable for animated picture technique.

Such a sequence simulating the ignition and growth of a flame, must start before zero time, i.e., before the passage of the ignition spark, in order that it may show the entire history of the flame. There is an inherent minimum delay in all the varitimers, such that dial zero is not zero time. In order to make a start of the record before zero time, recourse was had to two varitimers, one for the ignition gap and one for the illuminating gap. By appropriate setting of the two varitimers to handicap the fast one, a common pulse to the two could yield coincidence of the two sparks for the starting time. For photography of the sequence a Maurer Model 05 cine camera was used, fitted with a 25mm objective. With this choice of focal length, the 2 in. diameter schlieren field fitted nicely on the 16mm frame. The camera was driven by a motor with push button control for opening the shutter and for accomplishing single frame film advance.

The method of operation was simple—one person progressively advanced the varitimer dial for the correct time increment, and pressed the pulsing button, while the camera operator worked the shutter and film transport control. This procedure was carried out for all of the film strips. For example, for the film made to accompany this paper, strips of 200 frames each were made with time increments of 0.05 microseconds and a strip of 400 frames with time increments of 10 microseconds. When these strips are projected, they yield the same illusion that would be pro-

duced by a camera filming a single ignition at frame speeds of respectively 20 million, 2 million, and 100,000 frames per second.

This film sequence was made on Kodachrome. With respect to the color, the ignition spark is recorded by its own light. The color of the remainder of the photographic detail is the response of the Kodachrome emulsion to the light from the illuminating gap. The nature of the exposure is such that the light from the burning gas does not record on the film. Excerpts from this film are shown in Figure three. Note: (a) the appearance and development of the glow between the electrodes, (b) the separation and expansion of the shock wave, (c) the change in shape of the kernel from prolate to oblate ellipsoid, (d) the development of the toroid from the ellipsoid, and (e) the burning out of the center of the toroid to result again in a roughly ellipsoidal volume.

The equivalent camera-taking rates are 20 million frames per second for the first two strips, 2 million for the third strip and one-hundred thousand frames per second for the fourth and fifth strips.

The authors desire to acknowledge the assistance and cooperation of Mr. Nick Galminas of the Applied Physics Laboratory who loaned and operated the camera and handled the details of processing and editing the 16mm film.

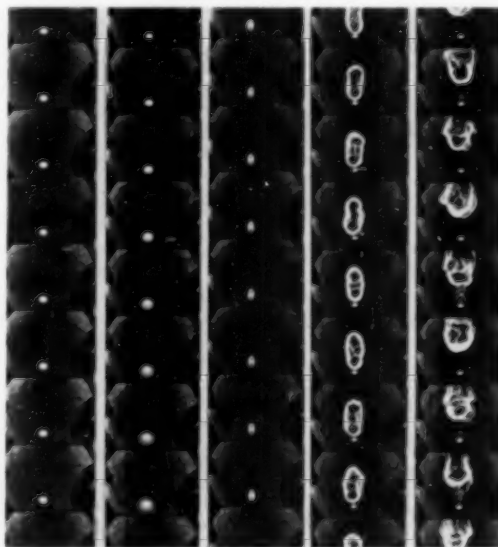


Fig. 3. Simulated motion pictures on 16mm color film made by progressively delayed timing. The equivalent camera taking rates are, for the first two strips, 20 million frames per second; the third strip 2 million frames per second; the fourth and fifth strips, one-hundred thousand frames per second.



# A NEW OPTICAL TECHNIC FOR IMPROVING EXPOSURE UNIFORMITY OF AUTOMATICALLY TIMED PORTRAIT PRINTS

John M. Centa\* and James D. Whiddon†

WITH CONVENTIONAL automatic roll-printers, exposure errors are usually caused by non-reproducible density "readings" of the phototube circuit, or by "incorrect" readings unavoidably made of unwanted negative portions. Such errors can now be avoided or reduced considerably by a modification of present photographic printing equipment.

Although new advances in phototube circuits have provided stable exposure control units which will render reproducible density readings and exposure control, the problem of quickly and accurately positioning on the phototube cathode the critical area of the portrait negative face has remained unsolved on currently available automatic printers.

A satisfactory optical technique has been developed by personnel of the Du Pont Company's Photo Products Department during recent studies of photographic negative scanning methods. A working conversion unit was designed, fabricated, and production-tested by personnel of School Pictures, Inc., Jackson, Mississippi.

A modification of the optical system of a Kodak Velox Rapid Printer Type IV was made to permit accurate pre-exposure positioning of the exposure-controlling beam splitter negative image on the cathode of a fixed position phototube. With this technique, print exposure uniformity is improved and remake rate is sharply reduced, thus increasing overall operator output. (The authors have undertaken no study of related patents or patentability).

The actual performance cycle of this modified optical system can best be illustrated by considering the steps in making a theoretical print on a converted Kodak Type IV Velox Rapid Printer.

In operating sequence, the operator slides the negative into the printing mask and simultaneously views the placement of the reflected beam splitter negative image on a target and aperture just in front of the fixed position phototube cathode. If it is seen that the proper negative face area will be "read" by the phototube aperture, the printer exposure cycle is initiated and proceeds in the normal fashion.

If, however, the operator sees that the phototube aperture will not "read" the critical negative area, the beam splitter image is shifted vertically, horizontally, or both, by turning two control knobs which adjust the angular position of tiltable beam splitter to obtain

proper negative-phototube aperture registration. When the negative image is thus properly aligned on the phototube aperture, the printer exposure cycle is started as usual. The actual operation of moving and centering the critical negative area on the phototube aperture is almost instantaneous—it takes far longer to describe the action than to do it.

Since the tilting of the beam splitter has no perceptible effect on the placement of the transmitted printing image, the goal of providing selective phototube "reading" of the exposure-controlling beam splitter image without affecting the printed image—and without appreciably increasing the printer time cycle—has been achieved. Production experience has shown that only five to fifteen percent of the average school photography roll negatives need positioning, but these are negatives which cause improperly exposed prints or actual print remakes.

Other modifications in the Type IV printer were made:

(a) To permit the operator to see the reflected beam splitter negative image by removing optical obstructions.

(b) To provide the bright, reflected beam splitter image necessary for adequate operator visibility.

(c) To retain adequate safelight protection for the printing paper.

Step (a) is achieved by using a special yellow negative viewing light source and by providing transparent safelight materials to take the place of the metal "capping" shutter in the original printer.

Steps (b) and (c) require the use of a special yellow-red reflecting, blue-green transmitting dichroic beam splitter. This unusual but inexpensive "mirror" has the unique characteristic of selectively reflecting a large percentage of the red-yellow "safe" viewing light to form a bright yellow previewing image (thus providing even greater safelight safety for the sensitized paper) while transmitting the blue and green light required to expose most photographic papers.

It is worthwhile noting that the original application of this tiltable dichroic beam splitter technique worked satisfactorily the first time it was assembled, and that modifications of it have been in continuous production usage ever since.

Details of the conversion of the Kodak Type IV printer are referenced to the following schematic drawing of the printer's optical path. Though an apology to Rube Goldberg is almost warranted as the operating sequence is described, it is felt that the interlocking relationship of the various changes can best be described in this fashion.

\* E. I. du Pont de Nemours & Company, Incorporated, Wilmington 98, Delaware.

† School Pictures, Inc., Jackson, Mississippi. Received 21 October 1954.

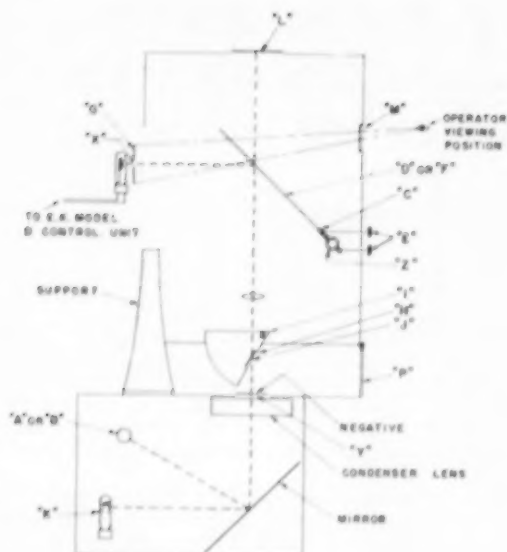


Fig. 1. Schematic side view (not to scale) of Kodak Velox Rapid Printer Model IV showing modifications of the optical path.

### Conversion Instructions

The basic equipment used in this technique is the Kodak Velox Rapid Printer Type IV and the new Kodak Model D exposure control unit.

1. Remount present fixed-position beam splitter holder "C" on a centered ball joint "Z" so that the splitter "D" can be tilted forward, backward and sideways with the screw adjustment arms "E". By tilting the beam splitter in this fashion, the reflected image on the phototube target "G" can be shifted over a wide vertical or horizontal range without appreciably affecting the placement of the transmitted printing image.

2. Replace the standard plain glass beam splitter "D" with a Libbey-Owens-Ford 90-720 dichroic red or similar reflecting mirror "F". These mirrors can be ordered from Liberty Mirror Division, of Libbey-Owens-Ford Glass Co., Brackenridge, Pennsylvania. Specify a mirror having a low reflection coating on the side opposite the dichroic coating. With this dichroic beam splitter, the photographically active blue and green light is transmitted during exposure to give maximum paper speed, while the photographically unimportant yellow-red component is reflected to activate the phototube circuit.

3. Place a white target "G" at the focal point of the reflected beam splitter image. Cut the desired aperture in the target "X" and position the phototube cathode from the model "D" unit directly in back of the aperture, so that only the selected negative area is read by the phototube.

4. Replace the white low-voltage negative viewing light in the lamp house "A" with a 60W yellow bug (insect repellent) bulb "B" operating at 110V. It may

be necessary to remove the glass diffusion plate from the lamp house and adjust the lamp socket to make room for this larger bulb. This change provides bright yellow light for negative viewing.

5. Cut an aperture "H" through the flap shutter "I" and cover the aperture with a yellow-red filter material "J" having 0.000 transmission below 5700 angstroms and 85 per cent or more transmission at wave-lengths higher than 5900-6000 angstroms (a Wratten 23A filter is satisfactory).

This flap shutter normally "caps" the lens at the end of the exposure cycle to prevent the sensitized paper "L" fogging from the afterglow of the exposing source "K". The filter insert "J" is fully effective in preventing this afterglow fogging, while transmitting a very high proportion of the yellow-red viewing light "B" output necessary to produce a visually satisfactory yellow-red beam splitter image on the phototube target "G".

6. Cut an aperture "M" through the front of the printer, so that the operator can sit in the usual printing position and directly view the reflected beam splitter (yellow-red) image on the phototube target "G" in relation to the phototube aperture "X". The viewing aperture "M" can be covered with a suitable filter material "J" to prevent white light scatter during exposure.

7. Hang a movable sheet of clear red plastic "P" from the front edge of the printer housing to reduce the light intensity of the previewing source to the operator's eye and to prevent excessive light scatter from the printer. This shield reduces operator visual fatigue by approximately balancing the light intensity of the viewing aperture and of the phototube target image.

In operating sequence, the operator places a negative in the negative aperture "Y", views the position of the yellow reflected image on the phototube target "G", turns the adjusting screws "E" to position the critical negative density area on the phototube aperture "X", then initiates the printer exposure.

During the automatic exposure cycle, the exposure source "K" lights, the flap shutter "I" swings out of the way, the blue-green light transmitted by the beam splitter prints the paper, the yellow-red light reflected off the beam splitter passes through the phototube target aperture where it is totalized by the phototube to terminate automatically the exposure, the flap shutter "I" closes, the paper feed advances, and the equipment is ready for previewing the next negative with the yellow safelight viewing source "B" lighted.

### Summary

Roll printing experience with a modified E. K. Type No. 4 printer has demonstrated that use of the optical technique described will provide more uniform portrait-type exposures, better average print quality, fewer print remakes and an overall gain in operator output (when the time formerly spent in reprinting rejects is considered).

There seems to be no reason why this same optical technique cannot be applied to other types of existent or proposed printers, where it is necessary to obtain selective phototube "readings" for optimum print quality.

# CELLULOSE ACETATE PRINTING FILTERS

W. L. Bostwick and E. S. Mackey\*

THE growth of color photography in recent years has promoted an increased demand for optical filters for photographic purposes. The requirements of color processes are such that several different types of filters are now made which were not in demand for black and white photography. These new filters include (1) the conversion filters, used either for exposure of daylight type color film under tungsten illumination or for exposure of tungsten type film in daylight; (2) ultraviolet absorbing filters; (3) color compensating filters in magenta, cyan and yellow or red, green, and blue for modification of light sources or correction of emulsion characteristics; and (4) conversion filters for various printing light sources.

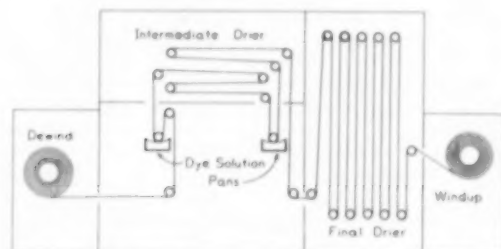


Fig. 1. Schematic diagram of dye imbibing and drying equipment for making cellulose acetate printing filter foils.

The types of photographic filters now in use may be classified according to their composition as:

- a) Plain or lacquered gelatin foils
- b) Glass—solid or laminated by means of a colored adhesive
- c) Solid plastic

Gelatin type foil filters are supplied in a wide range of absorption characteristics, but are fragile requiring very careful handling to avoid fingerprinting or heat buckling during long exposures. Moisture tends to cloud and swell this type of filter. Low abrasion resistance and susceptibility to mold growth are inherent with gelatin filters.

Glass filters are rugged as far as scratching and fingerprinting are concerned but, of course, are fragile and expensive. The choice of absorption characteristics is somewhat limited in the case of solid glass filters. Printing type filters are seldom prepared from glass since the use of several filters in a correction filter pack would result in a bulky, thick filter pile.

Plastic filters of methylmethacrylate, allyl diglycol-carbonate and polystyrene have limited use in certain printing applications but are expensive. These filters have much better scratch and moisture resistance than gelatin foils.

Dufay-Chromax Limited, England, makes cellulose

acetate filters in thicknesses up to 0.10 inch, and also cellulose acetate laminated filters but the range of the filters offered is quite small. These filters are not generally available in this country.

These filters may be lens grade or printing grade. The lens grade filters have surfaces of optical quality and are used over the lens or image—forming part of an optical system. The printing grade filters do not have surfaces of optical quality and are used primarily for modification of light sources. Although printing filters are not designed for lens application in critical work, picture sharpness is not appreciably affected if no more than one filter is used at one time.

Cellulose acetate printing filters are being manufactured and marketed in the United States in a wide range of color and density. The filters are quite rugged and are relatively insensitive to heat and moisture. They are easily cleaned and are resistant to mold growth.

The filters are manufactured by imbibing 5.5 mil thick cellulose acetate film stock with a solvent system containing a dye. This solution may be applied to one or both sides of the film stock. The solvent softens the film and permits the dye to be absorbed into the surface. A schematic diagram of a machine for manufacture of filters by this method is shown in Figure one. A cross section photomicrograph of an imbibed filter is shown in Figure two. The area of dye penetration can be readily noted along the top edge.



Fig. 2. Photomicrograph of an imbibed plastic filter foil showing the dye penetration into the cellulose acetate.

The imbibing procedure permits the manufacture of filters of varying density by adjustment of the dye concentration. Various color combinations may be easily made. For example, a cyan dye may be imbibed on one side and a yellow dye on the other side to produce a green filter. The travelling matte filters<sup>1</sup> used by professional motion picture laboratories are prepared by this method. A spectrophotometric curve of one of these filters is given in Figure three. Ninety different filters of this type have been prepared. This type of filter is sold only in professional motion picture film lengths coated with cine positive emulsion. They are

\* Ansco Division, Binghamton, New York. Received 19 November, 1954.

1. H. H. Duerr, "Ansco Color Negative-Positive Process," *Journal SMPT*, Vol. 58, pp. 465-479, June 1952.

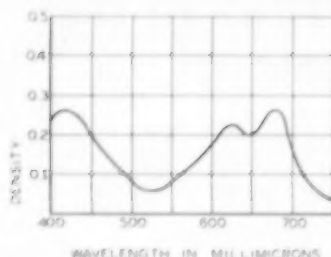


Fig. 3. Absorption curve for Ansco Traveling Matte Filter No. 0.20 green.

designed for use exclusively on high-speed continuous motion picture printers.

Color compensating filters with a wide range of absorption characteristics have been prepared for printing of color transparencies on color printing stock such as Ansco Printon or Color Duplicating Film. The filters are spaced uniformly in density from 0.025 to 0.50 and corresponding filters in different series are comparable. The filters have been identified by numbers representing the printing density of the filter. Spectrophotometric curves of these filters are shown in Figure four. Table one gives the relationship between the decimal series Ansco Color Compensating Filters and previous Ansco CC printing filters. Some of the decimal series are not identical in density with filters of the old series so the relationships shown are only approximate in some cases.

A very efficient ultraviolet absorbing filter has also been prepared by the imbibition technique. The ultraviolet absorbing dye is incorporated in the solvent system. Figure five shows the spectrophotometric characteristics of the UV 16P filter. This can be used for a variety of purposes including correction of printing light sources and as overlays to prevent light fading of color images.

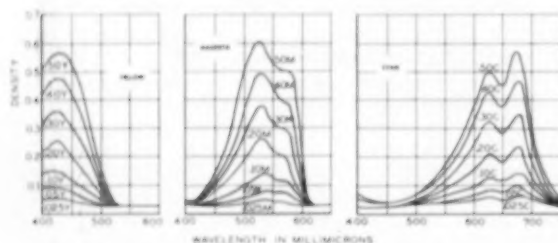


Fig. 4. Absorption curves for Ansco Color Compensating filters in the yellow, magenta, and cyan series, showing the spaced relationships.

The Ansco No. 11 Conversion filter is used to modify excessively blue light produced by cold light or fluorescent light sources. The spectrophotometric curve of this filter is given in Figure six. It is particularly valuable as it permits a reduction in the number of filters generally

Table 1  
APPROXIMATE RELATIONSHIP OF ANSCO COLOR COMPENSATING FILTERS, DECIMAL SERIES AND PREVIOUS SERIES

Cyan Filters		Yellow Filters		Magenta Filters	
Decimal	Previous	Decimal	Previous	Decimal	Previous
.025C = 43/2		.025Y = 23/2		.025M = 33/2	
.05C = 43		.05Y = 23		.05M = 33	
.10C = 44		.10Y = 24		.10M = 34	
.20C = 44 + 43		.20Y = 24 + 23		.20M = 35	
.30C = 45 + 43		.30Y = 25 + 23		.30M = 35 + 33	
.40C = 45 + 44 + 43		.40Y = 25 + 24		.40M = 35 + 34 + 33	
.50C = 45 + 45		.50Y = 26		.50M = 36	

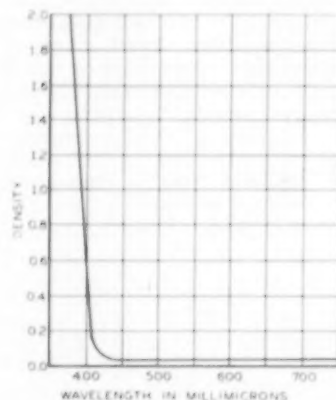


Fig. 5. Absorption of Ansco Color Printing Filter No. UV 16P.

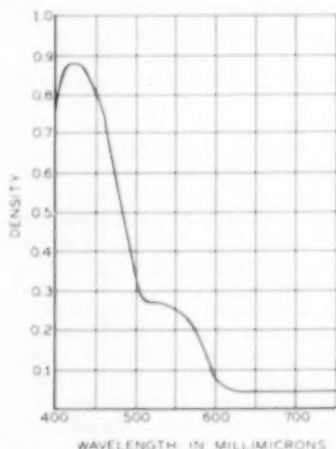


Fig. 6. Absorption of Ansco Color Printing Filter, Conversion No. 11.

used in the pack for exposing Printon or color duplicating film. This filter is also made of cellulose acetate by the imbibing technique.

The Ansco cellulose acetate printing filters can be used singly, or in combination, to introduce almost any



desired color correction in various phases of color photography. However, as with gelatin-type filters, it is best to use the minimum number of filters which will produce the desired correction because of light scattering

caused by a bulky filter pack. The improved physical characteristics of the cellulose acetate filters will permit the user who practices reasonable care in handling filters to utilize them indefinitely.

## PHOTOGRAPHIC SHORT CUTS IN ENGINEERING DRAWINGS FOR PIPING AND EQUIPMENT

H. A. Burns and W. R. Sutton\*

**T**HE USE of photography as a production or maintenance tool to save money in chemical process industries is often overlooked. With the present shortage of draftsmen and the comparatively high cost of making complete engineering drawings, it is imperative that short cuts be made in preparation for numerous piping alterations required to meet the constantly changing production conditions and improvements in manufacturing processes. It is almost axiomatic in the chemical process industries that, in spite of the best intentions, many of the existing drawings of process lines are out of date and in many instances these obsolete drawings are practically worthless for engineering purposes.

Photographs can be used as an aid in bringing the drawings up to date, especially for correcting flow charts. The draftsman can save many time-consuming trips to the field by photographing the piping and making corrections to the drawings using the photographs as reference.

Another use of photography can be made at the time when process piping must be dismantled for cleaning and later reassembled or altered. Photographs are much better because they are easier to read than regular drawings. Also they show the location of the hangers, the positioning of the valve handles, and other useful details that are usually omitted from engineering drawings. A special advantage is that less skilled men can be used as the need to be able to read blue prints is eliminated. This has a considerable advantage on rush jobs and during shutdowns the operators can be used on the mechanical crew to supplement the regular maintenance men. It is common practice for each length of pipe and fitting to be numbered before the dismantling is started. As many of the cleaning solutions will remove painted numbers, several industries are using aluminum or stainless steel bands with embossed numbers, which are easy to make and install. These bands provide a permanent marking which may be quickly removed, if necessary.

When piping systems are to be altered the changes can be indicated directly on the photographs but it is necessary to mark each print. The prints should be made on a paper having a matte surface, such as Ansco Brovira Kashmir, that will readily accept marking with a soft pencil or with ink.

If more than one print is required, which is usually the case, the marking of prints is a time consuming job and the marking of multiple prints may lead to errors. One way to eliminate marking multiple prints is to indicate the alterations on an enlargement and make a photo copy of it. This requires considerable skill and many companies do not have the special photographic copying equipment required.

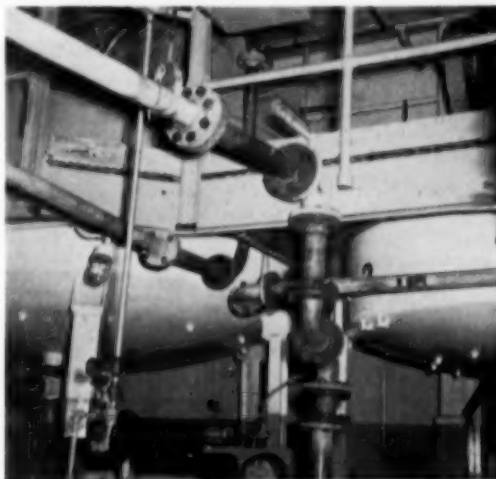


Fig. 1. Photograph of existing chemical process pipelines and equipment used as a basis for detailing engineering changes.

A faster and cheaper procedure is recommended when multiple prints are required. This method consists of using photographs of the existing piping with an overlay of Ozalid Sepia Foil showing the changes. The method of making these overlays is as follows: Enlarged 8" X 10" or 10" X 12" photographs of the existing equipment should be made. A sheet of tracing paper is placed over the photograph and the required changes drawn on the tracing paper. Only the changes should be indicated on the tracing paper, which can be done quickly free hand. The tracing paper is then removed from the photograph and an Ozalid Sepia Foil print made from the tracing. This transparent foil with its image of the structural changes should be fastened over

\* Production Engineering Department, Ansco Division of General Aniline & Film Corporation, Binghamton, New York. Presented as part of the Symposium on Engineering Applications of Photography preceding the PSA National Convention in Chicago, Illinois, 5 October, 1954. Received 1 October, 1954.

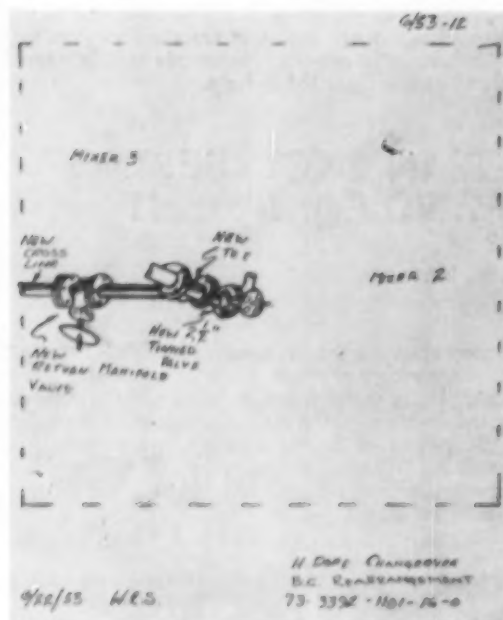


Fig. 2. Pencil sketch made on translucent tracing paper overlaying the photograph shown in Figure one to show the piping changes that are required.

the photograph by two wire staples in the upper corners so that it may be lifted to check the original layouts. In practice it is usually necessary to make at least three sets of prints, one for the field, the second for the Engineer and the third sent to the Drafting Room for record purposes.

A process engineer can usually indicate the required changes to the piping shown on a photograph in about 30 minutes. If complete new drawings of the piping system showing the interferences, such as columns, air ducts, sprinkler lines, etc. were made, it would take many hours. It is estimated that photographs with the foil over-lay showing the changes, cost less than one-tenth as much as making conventional drawings. The following is a specific case in a chemical industry and indicates the savings which can be accomplished using this procedure. About one month before a summer shutdown, it was decided to make extensive changes to some chemical process piping and to dismantle a major portion of all this piping for cleaning preparatory to conversion to a new chemical system. It was estimated that to make the required drawings would cost in the neighborhood of \$3,000 to \$4,000. Neither time nor manpower was available for the drafting work so the project engineer had photographs taken and made the foil overlays in a very few hours without interfering with his many other activities in connection with the project. A set of prints was given to the Drafting Room so that the drawing could be corrected later.

What has been said about photographing process piping holds as well for equipment being dismantled for cleaning, repair, or alteration. The equipment should be photographed from several angles before dismantling

is started and enlarged prints should be placed on the wall near the unit. It will then not be necessary to depend upon the memory of the mechanics and pipefitters when the equipment is reassembled to assure that the proper piping, lubrication, cooling water connections, etc. are made and that the guards, enclosures, counters, temperature recorders, etc. are replaced in their original positions.

No special photographic equipment is required for taking these pictures of process piping or equipment. If the company does not have a photographer on its staff, commercial photographers are usually available who will take these pictures for a very reasonable fee. In general, a camera with an  $f/3.5$  lens is adequate. It is advantageous to use a camera having a short focal length lens since it permits a wide field of view with maximum sharpness in both foreground and background, even when the subject occupies a considerable depth. High-speed press type films are unnecessary and in the case of very small negatives, undesirable. Ansco Supreme Roll-film, Ansco Isopan Sheet Film or equivalent is recommended, as negatives made from these films give extremely sharp enlargements, even from as small as  $2\frac{1}{4}$  inch square negatives. Flash illumination rather than flood lighting is recommended to eliminate the wiring problems and to save time. Flood lighting is slightly cheaper if the time spent photographing a job is not a major factor.

The picture (Figure one) was made with a  $2\frac{1}{4} \times 2\frac{1}{4}$  Ansco Reflex camera with Supreme roll film. The camera was mounted on a tripod. Most of the pictures were taken using only one flash bulb. Where there was a large amount of piping and shadows were deep, two spaced bulbs were used.

The use of *photographs* in place of mechanical drawings, while it is not new, is often overlooked as a means to save time and money. As far as the author knows, the use of Ozalid Sepia Foil overlays on engineering photographs is not widespread. It is a tool which, in chemical industries where there is always considerable changing of pipelines, can be used to cut costs and avoid delays.



Fig. 3. The Ozalid Sepia Foil, made from a pencil sketch, is stapled over the photograph and given to the mechanics who can readily visualize the piping changes and also consult the original photograph.

# ELECTROLYTIC RECOVERY OF SILVER FROM FIXING BATHS AT LOW CURRENT DENSITY\*

A. A. Rasch and J. I. Crabtree

## ABSTRACT

Electrolytic recovery of silver from fixing baths has been practiced by motion-picture processing laboratories for over twenty years, but the high cost of the available electrolytic cells and their large capacity have made the electrolytic system of little practical interest to most other processors of photographic materials. However, with the appearance on the market of smaller and cheaper electrolytic silver recovery units, general interest in the system has been revived. The principal problem involved is to plate out metallic silver without sulfiding the bath. The prevention of sulfiding depends on the control of several factors, including (1) current density, (2) degree of agitation of the fixing bath, and (3) concentration of the various components of the bath. These conditions are discussed in relation to (a) the successful operation of small electrolytic silver recovery units, and (b) the effect of the electrolysis on the photographic properties of the bath. The low current density silver recovery units can successfully remove silver from fixing baths on a long-term basis. The gross return on the recovered silver, should cover the cost of the unit, installation, operating, and maintenance costs, and the cost of handling, selling, and refining the recovered silver. Further savings might result from more efficient use of the fixing-bath chemicals, but not to the extent that has been mistakenly claimed in the past. No chemical savings can be expected in systems where exhaustion is caused primarily by dilution from carry-over. At best, chemical savings will amount to 20 percent with ammonium hypo baths and 40 percent with sodium hypo baths used to fix most amateur and professional films. In special cases when fixing silver-rich x-ray materials, savings up to 3 times to 4 times can be realized. Considerable savings may also result from electrolysis in certain fixing-bath systems for paper.

## OUTLINE

- I. Introduction
- II. The Chemistry of Electrolysis of Silver-Bearing Hypo Solutions
  - A. Reactions Occurring at the Electrodes
    1. Reactions Occurring at the Cathode
    2. Reactions Occurring at the Anode
  - B. Factors Controlling Efficiency of Electrolytic Plating of Silver from Fixing Baths
    1. Agitation
    2. Current Density and Silver Concentration
    3. Sulfite Concentration
    4. Gelatin Concentration
    5. Other Factors Affecting Electrolysis
      - (a) Type and Construction of Electrodes
      - (b) Temperature
      - (c) pH of the Fixing Bath
      - (d) Effect of Halides on Electrolysis
      - (e) Effect of Carried-Over Processing Solutions
      - (f) Sludge in the Fixing Bath
      - (g) Fixing-Bath Formula Variations
  - C. Composition of the Silver Plate Formed by Electrolysis of Fixing Baths
- III. Photographic Properties of Electrolyzed Fixing Baths
  - A. Changes Occurring During the Exhaustion of Unelectrolyzed Fixing Baths
    1. Silver Halide Concentration Build-Up
    2. Effect of Replenishment on Fixing-Bath Properties
  - B. Effect of Electrolysis on the Course of Fixing-Bath Exhaustion
    1. Ammonium Hypo Fixing Baths
      - (a) Amateur and Professional Roll and Sheet Films
      - (b) X-Ray Materials
    2. Sodium Hypo Fixing Baths
      - (a) Amateur and Professional Roll and Sheet Films
      - (b) X-Ray Materials
      - (c) Photographic Papers
    3. Use of Electrolysis in Replenished Systems
    4. Effect of Electrolytic Silver Recovery on Stability of the Processed Materials
    5. Other Secondary Effects of Electrolysis on Photographic Properties of Fixing Baths
      - (a) Halide Build-Up
      - (b) Build-Up of Anodic Oxidation Products
      - (c) Effect of Electrolysis on Hardening Action
- IV. The Economics of Electrolytic Silver Recovery
  - A. Potentially Recoverable Silver
  - B. Efficiency
  - C. Fixed Costs

- D. Net Profit and Labor
- E. Chemical Savings
- V. Summary
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## I. INTRODUCTION

The recovery of silver from exhausted fixing baths by electrolysis was first extensively investigated by K. C. D. Hickman<sup>1,2</sup> and his co-workers about twenty-five years ago and an electrolytic silver recovery cell was designed and operated successfully. Cells of Hickman's basic design have since been installed chiefly in motion-picture processing plants which may process up to 150 million feet of 35mm film a year when approximately 200,000 ounces of silver can be recovered from the used fixing baths.

Although Hickman's published work is extensively referred to in this and in other publications, credit should also be given to T. N. Ingman and F. E. Garbutt,<sup>3</sup> who pioneered in the electrolytic recovery of silver, and air-agitated cells of their design were operated effectively in motion-picture processing laboratories.

Since the publication of Hickman's investigations, many processors of photographic materials have periodically been interested in recovering silver by electrolysis. However, most processing plants did not approach the capacity of the motion-picture plants and the potential silver yield was not great enough to make it economically feasible to use the Hickman cell which is expensive in itself and involves high operating and maintenance costs.

As an alternative to electrolytic silver recovery, various other methods have been employed. Displacement of silver from a fixing bath with a more active metal, such as iron or zinc, has been used on a large scale by some motion-picture laboratories, particularly for "tailing," while the small-scale Gopher<sup>4</sup> recovery units operate on this same principle. A variation of the deposition process is employed in the galvanic units<sup>5,18</sup> currently available on the market. A second alternative involves various means of chemically precipitating the silver<sup>6</sup> and selling the silver-bearing sludge.

These methods have not been completely satisfactory for one or more of the following reasons: (1) too much handling is necessary; (2) in many cases it is not possible to re-use the stripped baths; (3) the customer must depend on the word of the refiner as to the value of silver recovered; and (4) the photographer has felt that he could realize a greater return by using the electrolytic process, thereby eliminating shipping, rental, and refining costs.

With the advent of semiautomatic continuous film-and-paper-processing machines, the capacity and number of large photofinishing plants have been considerably in-

creased and the possible savings from silver recovery and fixing-bath regeneration have become of greater interest to photographers. Furthermore, in recent years, an electrolytic silver recovery system known as the Purhypo Process has been developed and marketed by D. Pennellier & Company, Ltd., and its installation in photofinishing plants in Great Britain has lately been publicized.<sup>7</sup> A unit similar in operation has been devised by Henry O. Willier<sup>8</sup> and has been used in a few plants in the United States. More recently, a number of smaller units similar in operation for use in small-scale processing setups have been put on the market by a number of manufacturers. These include the Baker Electrolytic Silver Recovery Unit<sup>9</sup> and Argelic Electrolytic Units<sup>10</sup> available in England, while a similar model of the Baker Unit and the Fisher Silver Recovery Units<sup>11</sup> are available in the United States.

The major difference between all of these electrolytic units and the original Hickman electrolytic cell is that they operate at a much lower current density and, therefore, build up silver on a given area of electrode at a much lower rate. In this way it is not necessary to agitate the bath during electrolysis as is the case with the Hickman cell, and thus construction and operation of these units are simpler and the cost is lower.

Although quite a number of articles have appeared on the operation of these units, most have dealt only briefly with the chemistry involved, but the original results reported by Hickman and his co-workers do not wholly apply in this case. It is the object of this paper, therefore, to review the past work and to report on recent investigations on the chemical and photographic aspects of electrolytic silver recovery, particularly with reference to the low current density method.

## II. THE CHEMISTRY OF ELECTROLYSIS OF SILVER-BEARING HYPO-SOLUTIONS

Several reactions can occur during the electrolysis of a silver-bearing hypo solution other than the simple reduction of silver ion to metallic silver. The control of these reactions, and hence the design of the cell, determine how successfully silver can be removed in its elemental form.

### A. Reactions Occurring at the Electrodes

Hickman and his co-workers<sup>1,2</sup> extensively discussed the reactions occurring in an electrolyzed fixing bath with agitation and relatively high current density and, with some exceptions, their conclusions hold true in the absence of agitation and at lower current densities.

\* Communication No. 1694 from the Kodak Research Laboratories, Rochester 4, New York. Presented at the PSA National Convention in Chicago, Illinois, 6 October, 1954. Received 11 November, 1954.



1. *Reactions Occurring at the Cathode.* Most of the silver in an exhausted fixing bath is tied up as a silver thiosulfate complex ion. However, a small amount of free silver ion is yielded by the dissociation:



When electrodes are placed in the silver-bearing fixing bath and current of a suitable value is passed through it, the silver ion is reduced at the cathode:



At the same time thiosulfate and tetrathionate ions present will be competing for electrons at the cathode:



Two things are immediately obvious: (1) Since the silver ion is tied up in the negatively charged thiosulfate which will migrate away from the cathode, the concentration of silver ions at the cathode surface can be very low; (2) if reaction (3) occurs to any degree, the sulfide ion formed would immediately precipitate the silver as silver sulfide:



As has been found, the sulfiding reaction readily occurs in baths electrolyzed under the wrong conditions, with the result that plating ceases and the fixing bath is ruined. Therefore, the prevention of this reaction is the necessary adjunct to efficient electrolytic silver recovery.

In addition to deposition of silver, gelatin degradation products dissolved from the emulsions processed in the fixing bath will also "plate" out at the cathode and, although only a small quantity (2-5%) of these products may be plated out in comparison to the silver, they are necessary for successful silver plating.

2. *Reactions Occurring at the Anode.* At the anode, oxidation reactions occur which result in lowering the concentrations of thiosulfate and sulfite ions. However, quite a number of products can be formed through these reactions as, for example, the formation of tetrathionate and sulfate from the thiosulfate and sulfite, respectively.



Hickman also reported the formation of tri- and pentathionate ions while the authors can also add elemental sulfur to the list which, in some cases, was formed near the anode even while good silver plating was being obtained at the cathode.

The polythionates formed are known to be quite unstable. They can decompose to form other thionates or react further with thiosulfate or sulfite still present in the fixing bath. The latter possibility is amply demonstrated by the fact that considerably more equivalents of sulfite, thiosulfate, and silver are used up during electrolysis than would be predicted from the current passed through the solution, as is shown in Table I.

Present investigations were limited to noting only the effect which these electrode reactions had on the silver, thiosulfate, and sulfite concentrations in an

electrolyzed bath. At the same time, the conditions controlling the extent of these reactions and promoting one in preference to another were studied.

## B. Factors Controlling Efficiency of Electrolytic Plating of Silver From Fixing Baths

1. *Agitation.* At the outset, electrolysis of fixing baths was considered completely impractical since most of the early tests, such as those described by Crabtree and Ross,<sup>6</sup> resulted in the precipitation of silver sulfide in all cases except when very low current densities were used. Later Hickman found that silver could be plated at what was considered a reasonable current density if a high enough degree of agitation in the vicinity of the electrodes was used. Until recently, therefore, emphasis has been primarily on agitation as the major factor promoting successful silver plating.

At a current of 1.5 amperes, silver is theoretically deposited on the cathode of an electrolytic cell at the rate of a little over 6 grams per hour. Since a square foot of most types of photographic films will yield 0.4 gram or more of silver to the fixing bath, it is not surprising that the earlier workers were primarily interested in relatively high plating currents. At the same time, practical space limitations restricted the total electrode area, with the result that an electrolytic cell having a reasonable capacity was required to operate at a current density of 1 ampere per square foot or higher.

By using this prerequisite current density, on an experimental basis, and stationary electrodes in an unagitated silver-bearing fixing bath, it is found that at first a brownish silver plate forms on the cathode. As electrolysis proceeds, the plate darkens and turns black, owing to the formation of silver sulfide. With the formation of more sulfide ion, the bath turns black from the fine silver sulfide precipitate formed.

This condition is a result of silver ion being removed from solution at the surface of the cathode at a rate considerably faster than it is being supplied by the ionization of the negatively charged silver thiosulfate complex, and, as the silver complex migrates away from the cathode, the supply of silver ion is diminished even more. Consequently the much more abundant thiosulfate ion present at the cathode is reduced to sulfide ion which poisons the plate and eventually ruins the bath.

The obvious answer to the problem is to prevent the local drop in silver-ion concentration by agitation, but considerable agitation of the bulk of the solution is required to maintain the silver-ion concentration at the surface of the cathode. It was found, for example, that the agitation provided by a magnetic stirring bar in a cell containing 500 milliliters of solution served only to extend the brown plating period slightly when operating at a current density of 1.5 amperes per square foot on a 6-square-inch cathode. Increasing the agitation through the use of a small, stirring propeller gave some improvement in plating as did the use of a pump to recirculate the solution through the cell. However, these methods did not provide uniform agitation over the whole surface of the cathode, so that sulfiding would still occur in the relatively stagnant areas on the plate surface.

These examples serve to illustrate the somewhat difficult problem of agitation which Hickman effectively

Table I

EQUIVALENTS OF CHEMICALS OXIDIZED AND REDUCED IN ELECTROLYZED FIXING BATHS COMPARED TO THE THEORETICAL VALUES

Run No.	Equivalents Silver Reduced (X1000)	Equivalents Hypo Oxidized (X1000)	Equivalents Sulfite Oxidized (X1000)	Total Equivalents (X1000)	Theoretical Total Equivalents (X1000)
1	28	29	34	91	72
2	42	65	50	157	86
3	28	32	31	91	54
4	43	45	53	141	96

solved by an interelectrode paddle wheel system in which the surface layer of solution at the electrode was continually swept away. Cells employing this means of agitation have been used successfully for many years, but are necessarily costly to build and their use has been limited almost completely to the large motion-picture film processing laboratories.

Two other systems which provide agitation of an intermediate degree between no agitation and that given by the paddle wheel are (a) agitation with air, and (b) the use of a rotating cylindrical electrode. Thus, Kare M. Heiberg<sup>12</sup> reported obtaining satisfactory plating with air agitation in the moderate current density range, although he favored vigorous mechanical agitation for best results.

The air agitation method in particular offers the advantage of a much more simplified apparatus, but careful design must be employed so that the agitation provided is even throughout the cell. If there is a tendency for channeling, then relatively stagnant areas of the cathode will eventually sulfide. Also, with this form of agitation the maximum tolerable current density level is lower than is permissible with the paddle wheel system.

A rotating electrode has also been found practical but an electrolytic cell of this design is just as costly as one fitted with paddle wheels.

2. *Current Density and Silver Concentration.* Having established a suitable method of solution agitation, Hickman found that current density could be varied over a wide range, depending on the silver concentration, without causing sulfiding. Furthermore, with all other factors kept constant, he found that at densities of the order of 1 ampere per square foot, almost all of the silver could be successfully removed from the bath. In other words, the higher the silver concentration, the higher would be the permissible current density. For example, in an acid sodium hypo fixing bath containing more than 6 grams of silver per liter, a current density of 8 amperes per square foot could be used to plate out the silver before sulfiding occurred.

Hickman did not extend his investigation of the relation of current density to silver concentration to systems having lower degrees of agitation, since it did not appear to have much practical interest. Therefore, it was not until 1937, when a British patent was granted to Henri Georges Doffin,<sup>13</sup> that information was available on low current density methods of electrolysis. Doffin noted that a good silver plate could be obtained from an electrolyzed fixing bath with no agitation when the potential drop across the electrodes was maintained at a value slightly below what he called the "critical voltage" (decomposition voltage) for a bath of given composition. This

critical voltage value ranged from 0.25 to 0.50 volt depending on the type of bath. Translated into terms of current density, the values ranged from 20 to 40 milliamperes per square foot. Under these conditions, the sulfide-forming reactions would not occur, even in baths containing 0.1 gram of silver per liter or less.

In the absence of agitation, a recovery cell need consist only of a sheet cathode and suitable anodes (graphite or carbon) hung directly in the fixing tank and a potential applied across them to give a suitably low current. Practical application of this method was made by the Pennelier Co., Ltd., in England who evolved the Purhypo System.<sup>7</sup> In the United States, a similar system devised by Henry O. Willier<sup>8</sup> has been used to a limited extent. Recently several articles have appeared on the operation of the Purhypo unit which have served to revive interest in electrolytic silver recovery methods.

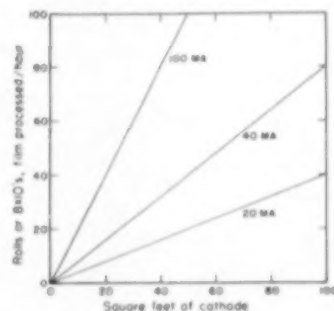


Fig. 1. The curves show the effective area of cathode necessary to plate silver at the rate at which it enters the bath, using the low current density range of from 20 to 100 milliamperes per square foot.

The advantages of simplicity, low cost, and ease of operation of such units are obvious. However, the one major disadvantage is size. At a current density of 20 milliamperes per square foot, it would require  $2\frac{1}{2}$  square feet of cathode area to recover the silver yielded by one 8-x10-inch film in 1 hour. Figure one illustrates the large areas of cathode necessary to recover silver supplied by various quantities of developed film at a rate equivalent to that at which it enters the bath. It is therefore necessary to make some compromise and recover silver at a considerably lower rate than that at which it enters, but, even so, pictures of some of the larger units mounted exterior to the fixing tanks show sets of electrolytic cells filling a small room. Round-the-clock operation of such units however serves to reduce

the silver build-up that occurs when actually processing film.

Recently other smaller units of the same general design have been put on the market. The size and capacity of these indicates that they operate at considerably higher current densities than those suggested by the Doffin patent and yet manage to recover silver successfully without recourse to agitation. It is for this reason that the present authors have studied the plating conditions in the range of current densities between those studied by Doffin and Hickman.

The apparatus used for many of the current density and other tests is shown in Figure two. The unit consists of six cells connected in series. The cathodes have a plating area of 6 square inches and are of stainless steel. The back sides of the plates are coated with an insulating material, such as asphaltum, to prevent the plating that would otherwise occur on the side away from the electrode. The anodes are  $\frac{3}{8}$ -inch carbon rods placed  $\frac{1}{2}$  inch away from the cathode. Current is supplied by a D-C rectifier and controlled through a power transformer on the rectifier and external rheostats. Current and voltage measurements are made continuously with the multimeter connected in the circuit. With this setup, it was possible to make simultaneous electrolysis of a series of similar fixing baths in which one component was varied.

In all of the tests made, except when otherwise stated, silver was added to the fixing baths by fixing unprocessed photographic emulsions.

Surprisingly enough it was soon found that considerably higher current densities could be employed to plate silver successfully from most baths than is indicated by the Doffin patent and the subsequent literature. How-

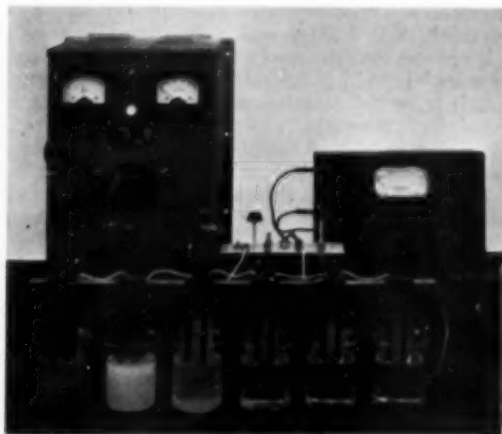


Fig. 2. Apparatus used for electrolysis experiments. Direct current is supplied to the series of cells in foreground from rectifier and control box shown behind the cells. Actual plating current is read on multimeter in right background. The experiment illustrated shows the effect of varying sulfite concentration on the quality of silver plating at a given current density. Solutions increase in sulfite content from left to right, 1.25-15.0 grams per liter. In the low sulfite solutions, the plates have sulfided, and bad sulfiding and sulfurization of the bath have occurred. High sulfite has maintained a clear solution and satisfactory plating.

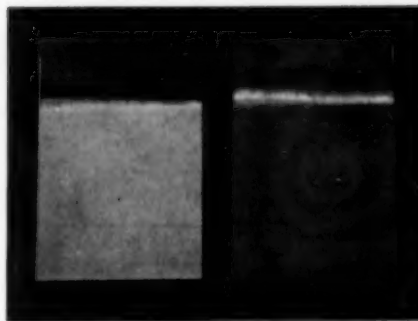


Fig. 3. The two cathodes illustrate the two extremes of quality of silver plate obtainable in low current density electrolysis. The left plate was obtained under conditions of low current density from a bath high in silver and sulfite concentration. The plate on the right was obtained under maximum current density conditions. If current density had been increased, the plate would have turned completely black.

ever, it is necessary to be cautious about stating maximum current densities and minimum silver concentrations for each type of fixing bath for a number of reasons:

1. The dividing line between good and bad plating was not clear cut. Good plating could be obtained from baths low in silver for short periods of time at a relatively high current density. In a longer period of electrolysis with all conditions kept constant, the quality of the plate gradually deteriorated with eventual sulfiding of the bath.

2. It is difficult to say what is considered good and bad plating. There can be a wide range of current densities at which continuous plating can be accomplished without causing breakdown of the bath, while the color of the plate will range from slightly off-color to brown. Figure three shows the nature of the silver deposit obtained over a current density range from 0.3 to 1.0 amperes per square foot.

3. The current density-silver concentration figures pertain only to a given type of bath at one stage in the electrolysis. Since the composition of the bath other than the silver content is continually changing by virtue of electrolysis and film processing, as discussed below, it is impossible to give one figure to cover all conditions.

With this in mind, values of possible operating current density are given in Table II for various baths containing over 8 grams per liter of sodium sulfite and at least 0.5 to 1.0 grams of silver per liter which are electrolyzed in cells using graphite or carbon anodes and stainless-steel cathodes. These figures are based on many experiments made with the apparatus described and in practical tests made with larger silver recovery units and long-term electrolysis.

Good silver plating has been obtained on a short-time electrolysis basis with considerably higher current densities than are shown in Table II under conditions of no agitation. For example, it was found possible to obtain a nonsulfided plate from an acid ammonium hypo fixing bath at a current density up to 1.5 amperes per square foot, and a current density up to 0.75 ampere per square foot has been used successfully with acid sodium hypo baths. Perhaps, if it were possible to constantly

Table II

CRITICAL CURRENT DENSITY RANGE FOR THE ELECTROLYSIS OF VARIOUS FIXING BATHS\* (NO AGITATION)

	Amps. per Sq. Foot
Acid ammonium hypo fixing baths	0.20-0.40
Acid sodium hypo fixing baths	0.10-0.20
Alkaline ammonium hypo fixing baths	0.10-0.20
Alkaline sodium hypo fixing baths	0.05-0.10

\* For baths containing not less than 0.5 gram per liter of silver or less than 8.0 grams per liter of sodium sulfite.

maintain the exact composition of the fixing baths and condition of the silver plate, continuous electrolysis could be made at these higher current densities, but under practical conditions this is impossible.

The difference between the critical current density values for sodium and ammonium baths is quite marked, as shown by the data. The reason for this is not known, and remains to be determined. The simple substitution of ammonium hypo for sodium hypo in a formula without changing the other components other than to adjust the pH of the bath, would indicate that the ammonium ion was causing the effect. However, even very low concentrations of impurities are known to affect plating processes markedly, and the impurities in the commercial grade of ammonium hypo used in these tests were not known.

The discussion so far would at first indicate that Doffin was overly conservative in his figures for critical current density but, on further investigation, it is found that his figures are probably more realistic in the absolute sense, and can be interpreted as being the critical current density for good silver plating for any condition and type of fixing bath. The current density figures in Table II are applicable to practical silver recovery but they still depend on the control of other factors as follows:

3. *Sulfite Concentration.* In all of the past work, the presence of sulfite ion in the fixing bath has been found necessary to insure good silver plating under any conditions. Its function during electrolysis is much the same as when used to prevent the chain of reactions that occur in simple thiosulfate solutions when acidified. Cathodic reduction of thiosulfate, as shown in reaction 3, results in the formation of sulfite and sulfide ion. The presence of excess sulfite in the fixing bath, therefore, either inhibits this reaction, thus allowing the silver reduction reaction to predominate, or it participates in an almost instantaneous reaction with the sulfide to re-form thiosulfate.

As already pointed out, however, the oxidation of sulfite to sulfate is one of the reactions that can occur at the anode. Hickman's experimental results indicated that this reaction does occur during electrolysis but not to the same extent that thiosulfate is oxidized to tetrathionate. If the sulfite-sulfate reaction predominated the bath would become more acidic, as can be seen from reaction 6, which was not the case in Hickman's experiments.

In the case of the non-agitation, low current density experiments made by the authors, the anodic reactions are apparently more complicated. The baths became more acid with electrolysis and sulfite concentration dropped at an appreciable rate.

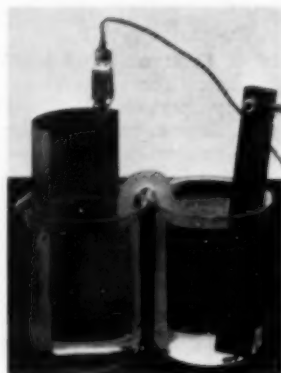


Fig. 4. The effects of anode and cathode reactions on fixing-bath composition during electrolysis were separated using this apparatus. Electrical connection between anode and cathode solutions is made by the salt bridge containing gel of 3 percent agar in saturated potassium chloride. The cathode is of 1/32" Type 316 stainless steel (left) and the anode consists of a graphite stick (right).

To study the anodic reactions more carefully, the apparatus shown in Figure four was used. The reactions occurring at the anode and cathode were separated by placing the electrodes in separate solutions, with the two half-cells thus formed connected by a salt bridge consisting of agar gel saturated with potassium chloride. Suitable covers were sealed over the tops of the cells to minimize the possibility of aeration effects. The cells were charged with a silver-bearing fixing bath, a suitable current was passed through the cells, and changes in solution composition were followed by periodic analysis.

The results of one of these experiments are given in Figure five and Table III. As can be seen, both sulfite and thiosulfate are used up at approximately equal rates. However, the total equivalents of sulfite and thiosulfate oxidized are more than twice the chemical equivalent of the current put through the bath. The exact mechanism through which this occurs is not known but it appears that the products formed by anodic oxidation react with either the sulfite or the thiosulfate ions, and this secondary reaction continues to occur even after electrolysis is stopped.

The solution from the anode compartment used in this experiment was stored in a stoppered bath. After 1 week, thiosulfate and sulfite concentration were still dropping, and in 2 more days, elemental sulfur had precipitated in the solution.

There was a small drop in sulfite concentration in the cathode compartment while the thiosulfate concentration remained unchanged. Hickman proposed that such a loss is due to reduction of the sulfite to hydrosulfite which, in turn, is either immediately reduced to thiosulfate or forms the same end product by bimolecular decomposition. However, the primary reaction at the cathode is the reduction of silver ion, as shown in Table III.

Many other experiments have, in all cases, shown a similar drop in sulfite concentration during electrolysis and, if it is allowed to continue for a long enough period, eventual sulfiding of the plate occurs. Again, no single critical concentration of sulfite which will prevent sulfiding of the silver plate and the fixing bath can be given since it will depend on the other factors of silver concentration and current density at the cathode. However, the following information can serve as a guide.



Table III

THE RATE OF OXIDATION AND REDUCTION OF VARIOUS COMPONENTS OF A FIXING BATH DURING ELECTROLYSIS

Millifaradays of Current	Milliequivalents of Silver Reduced at Cathode	Milliequivalents of Sulfite Lost at Cathode	Milliequivalents of Thiosulfate Oxidized at Anode	Milliequivalents of Sulfite Oxidized at Anode
15.9	14.5	2.2	8.1	11.0
31.6	30.3	3.8	24.2	32.8
47.8	42.5	8.0	45.2	52.8

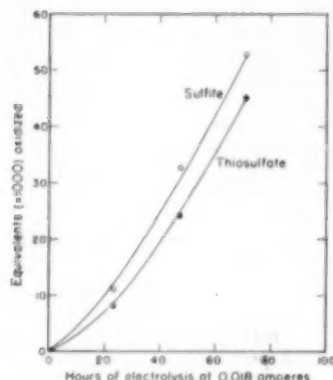


Fig. 5. Rate of anodic oxidation of sulfite and thiosulfate during electrolysis of a fixing bath. Curve 1: sulfite ion; Curve 2: thiosulfate ion.

In an acid fixing bath containing between 1 and 5 grams of silver per liter electrolyzed at normal current densities (see above), good plating is obtained when the sulfite concentration (as sodium sulfite) exceeds 8 to 10 grams per liter. At lower sulfite concentrations, the plate deposited becomes increasingly brown in color. When sulfite concentration is of the order of 3 to 5 grams per liter, bad sulfiding of both the solution and the plate occurs. In some cases when the silver concentration was high, good plating was obtained even at these low sulfite concentrations. Little or no silver sulfide formed and, instead, elemental sulfur was precipitated in the bath. This was apparently due to an anodic reaction since the first traces of sulfur appeared in the solution around the cathode. This would indicate that sulfite also acts as an inhibitor to certain anode reactions.

In terms of practical electrolytic silver recovery, the sulfite concentration must be maintained to insure continuous good plating. The larger silver recovery units are generally installed in systems where continuous replenishment of the fixing bath is maintained, and, in such cases, the sulfite in the replenisher is sufficient to maintain a high enough concentration. The smaller silver recovery units, however, will probably find their most extensive use in systems where periodic dumping of the fixing baths is used instead of replenishment. Even in these cases, carried-over sulfite-bearing solution from the preceding baths at least partially maintains the sulfite concentration, but, depending on the rate of electrolysis, some additional replenishment with sodium sulfite is usually necessary to insure good silver plating throughout the life of the bath.

Figure six shows how the sulfite and hypo concentration changed during the course of a practical test of

an electrolytic silver recovery unit of the Baker or Oscar Fisher type. The unit was operated at 0.4 ampere and run continuously for 30 days in 10 gallons of ammonium hypo fixer which was not replenished. Film was fixed in the bath at an average rate of three hundred 8-x10-inch sheets per week. Hypo concentration fell off gradually owing primarily to dilution by carry-over. However, the sulfite concentration fell at a disproportionate rate and it was necessary to replenish the bath at intervals with sodium sulfite (as shown by the vertical breaks in the sulfite curve). Just before replenishment in each case, the silver plate was darkening, irrespective of silver concentration. The addition of the sulfite improved the condition of the plate within a few hours.

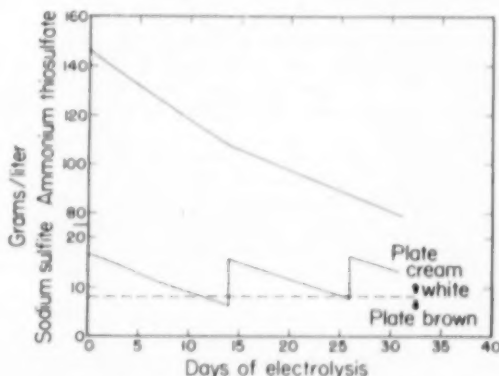


Fig. 6. The changes in fixing-bath composition during electrolysis are shown by the two curves. Sulfite concentration dropped off at a disproportionate rate, making it necessary to replenish with sodium sulfite to maintain fixing-bath quality. Electrolysis was made on a practical basis in 10 gallons of Kodak Rapid Liquid Fixer of an x-ray processing system.

When the same unit was in operation at the same current in 6 gallons of fixer, it was necessary to replenish with sodium sulfite at more frequent intervals; while it was operated at lower current density in the larger volume of solution, the intervals between replenishment were longer. Table IV shows the replenishment schedule that would be necessary for various operating currents in various volumes of fixing bath. It should be pointed out that when the silver recovery unit removes silver from the bath at a rate considerably lower than that at which it enters, the sulfite brought into the bath from carry-over is sufficient to maintain good plating.

Table IV

INTERVALS BETWEEN REPLENISHMENT TIMES FOR  
MAINTAINING SULFITE CONCENTRATION DURING  
ELECTROLYSIS\*

Capacity of Fixing Tank (Gal.)	Amperes Operating Current of Silver Recovery Unit (24 Hours per Day)				
	0.2 Amp.	0.4 Amp.	1.0 Amp.	1.5 Amp.	2.0 Amp.
5	8 days	4 days	2 days	1 day	...
10	17 days	8 days	3 days	2 days	2 days
20	34 days	17 days	7 days	4 days	3 days
40	...	33 days	13 days	9 days	6 days
50	...	...	17 days	11 days	8 days
70	...	...	24 days	15 days	12 days

\* Under the following conditions:

1. Replenishment rate = 19 grams of sodium sulfite per gallon.
2. Silver is being removed at an average daily rate of not less than half that at which it enters the bath.
3. The fixing bath is not otherwise being replenished.

4. *Gelatin Concentration.* The control of current density, and silver and sulfite concentrations are the more obvious factors insuring successful silver plating, but, less obvious, is the role that gelatin plays in the electrolytic process. Hickman found that different results were obtained if silver was supplied to the fixing bath simply by adding silver halide, as compared to exhaustion with film. In the former case, good plating would be obtained at the start of electrolysis but it soon deteriorated, with eventual sulfiding even though the necessary conditions had been maintained. He soon found that the small amount of gelatin and gelatin degradation products dissolved from the film were promoting good plating.

Gelatin is plated out on the cathode along with the silver in a concentration of about 2 percent, and apparently modifies the condition of the silver plate. In its absence, a highly crystalline plate is formed, and even under the high agitation conditions used by Hickman, enough silver-poor solution was trapped in this rough crystal surface to cause sulfiding.

The presence of a small amount of gelatin products in the bath prevented this condition but, on the other hand, a relatively high concentration of gelatin products again produced sulfiding conditions, probably because the amount plated out again caused silver-poor areas on the plate.

In recent experiments using low current density and no agitation, the beneficial effect of gelatin degradation products was not very evident. The plate obtained from baths supplied with silver from film was only slightly better than that obtained from gelatin-free baths. The physical appearance of the plate was the same matte, cream-white colored, type typical of electrolysis under these conditions. Since the amount of agitation provided by convection is very low, the necessarily low current used is not enough to deplete the silver in the solution trapped in the crystalline surface at a rate fast enough to cause sulfiding of the plate.

Experiments have shown, however, that excess gelatin will cause eventual sulfiding even at these low current densities. The occasion when actual sulfiding occurs is usually preceded by a fairly long, brown-plating period. These results have been confirmed in both small scale and low-term practical tests.

In practice, the gelatin build-up in the fixing bath is quite slow, requiring the processing of many sheets of film before it affects the electrolysis. First signs of brown-plating that cannot be cured by sulfite or silver replenishment appear when the bath has been exhausted to at least two-thirds of its normal life. At this point stopping the electrolysis over, say, a weekend when usually no film is being processed, can result in improved plating when electrolysis is restarted. Evidently in this period the gelatin is hydrolyzed to the extent that it no longer acts as a plate poison.

Towards the end of the useful life of the bath it is not possible to prevent browning of the plate by the means just mentioned. At this point, if the hypo concentration of the bath allows further exhaustion, plating can be improved by the addition to the bath of small amounts of certain compounds known as plate "doctors." Good results were obtained by the authors on adding thiourea to the bath in a concentration of 0.05 gram per liter. Hickman lists, along with thiourea, allyl and phenyl thioureas, thiocarbanilide, thioacetamide, and phenyl isothiocyanates as effective doctors when used at similar or even lower concentrations.

The need to use these compounds will depend, as always, on the use of the fixing bath. If highly hardened emulsions, as in the case of many roll films, are processed, the gelatin concentration will probably not reach the dangerous level. Conditions will also vary with the type of fixing bath. Replenishment will probably eliminate the need to use the doctors and, since most unreplenished baths reach the end of their useful life by the time the brown-plating becomes too objectionable, the use of these compounds can be avoided in most cases.

5. *Other Factors Affecting Electrolysis.* The primary emphasis has been placed on current density and silver, sulfite, and gelatin concentration since these interdependent variables control effective electrolytic silver recovery over a wide range of conditions. A number of other factors also have an effect but to a lesser extent, as follows:

(a) *Type and Construction of Electrodes.* In all the experiments described thus far, graphite anodes and Type 316 stainless-steel cathodes were used in the electrolytic cells. This combination has been found most satisfactory to date.

The choice of material for the cathodes is dictated primarily by its resistance to corrosion. In solution the cathode can be considered to be silver once the plating has begun. However, the portion above solution must be resistant to the corrosive action of the vapors of the fixing bath and the solution splashed on it. Stainless steel has been found most satisfactory for this purpose since its anticorrosion properties permit its use in any of the types of fixing baths, including those containing ammonium hypo.

The choice of anode material is, unfortunately, restricted to carbon or, preferably, graphite. Since oxidation reactions occur at the anode, few metals exist that will not corrode in the fixing bath under these conditions. Stainless steels have been used as anodes in silver recovery cells and have at first operated satisfactorily, although there is a higher potential drop

across the cell than when graphite is used.<sup>2</sup> When electrolysis is continued for any length of time, black, scaly patches form on the anode, especially at the solution-air interface. As the patches become larger, sulfiding occurs at these spots, resulting in spoiling the silver plate and the bath. The rate of corrosion is quite fast in fixing baths containing ammonium hypo, holes developing in 1 to 2 weeks in  $\frac{1}{16}$ -inch Type 316 stainless-steel anodes operated at a current density as low as 0.1 ampere per square foot.

The stainless-steel anodes function better in sodium hypo baths, but eventually corrode. This fact eliminates the possibility of saving space and using the steel fixing tank itself as anode for smaller units hung directly in the fixing tank. Experience with the larger high current density silver recovery units has shown that it is necessary to ground the fixing tanks and plumbing connected to the cell to prevent corrosion, even though there is no electrical connection.

Some tests were made with titanium anodes which resist corrosion very well. However, they were not suitable because the protective oxide coating formed on them during electrolysis increased the electrical resistance of the electrodes to such a degree that the flow of current was impaired excessively.

Graphite does not corrode appreciably during electrolysis and has a minimum resistance. Its major disadvantage is its brittleness, necessitating bulk to give enough structural strength.

The shape, relative area, and position of the electrodes in relation to each other did not have too great an effect on the silver plating. The size of the cathode, or more accurately the surface area, is calculated from values of maximum current density and total current under which the cell will be operated. However, the shape, whether in the form of sheets, strips, or screening, did not affect the quality of the silver plate when used in low current density units not requiring agitation. Fairly flexible cathodic sheets have been found most convenient, since flexing the silver-laden electrodes aids greatly in removing the silver.

The size of the anodes has been varied from an area equal to that of the cathode down to one-fifth the area without affecting the plating. However, Dolfin<sup>13</sup> recommends anode areas approximately the same as that of the cathode to avoid excess anodic voltages and to give more even control of voltage. Experiments have shown that uneven plating will occur in the long run where there is too great a discrepancy between the sizes.

For reasons of compactness, anode and cathode should be placed as closely together as possible, only enough space being left for a suitable build-up of plate. Varying the distance between the electrodes from  $\frac{3}{8}$  to  $\frac{3}{4}$  inches did not appear to have an appreciable effect on plating characteristics nor on the uniformity of the silver deposit, even when the anode covered only a portion of the cathode. The electrical resistance of the cell did not change measurably when the distance was varied to this degree.

(b) *Temperature.* Hickman found that maximum tolerable current density for obtaining good silver plate increased with increasing temperature in the range 25–60 C (77–140 F) but did not give any definite figures. Most of the low current density experiments of the authors were made in the range of 20–35 C (68–90 F) and no

appreciable change in plating characteristics was noted.

(c) *pH of the Fixing Bath.* It has already been shown that maximum tolerable current density for good continuous plating is lower for alkaline than acid fixing baths but there does not appear to be too much variation over narrower pH ranges. When electrolysis is carried on near the maximum tolerable current density in a given bath, the condition of the plate does not change appreciably with pH values below 5.0. When the pH of the bath is raised to 5.0–6.0, plating will not be as good and long-term electrolysis at the same current density would probably be unsuccessful. Above a pH of 6.0, lower current densities must be used or sulfiding occurs almost immediately with the start of electrolysis. Generally the critical maximum current densities are about halved when an acid bath is made slightly alkaline.

It is also interesting to note that current efficiency from the standpoint of the amount of silver plated varies considerably with pH, particularly when the fixing baths are agitated during electrolysis. When no agitation is used, current efficiencies are above 85–90 percent, even with the acid baths. In alkaline baths, current efficiencies are above 95 percent.

When agitation is used with an acid fixing bath, current efficiency drops considerably. Electrolysis experiments made with a cell using a fairly high degree of agitation and with the normal acid hardening fixing bath resulted in current efficiencies of 30–40 percent. With the same unit and using an alkaline fixing bath but electrolyzing at one-fourth the current density, a current efficiency of 80–90 percent was obtained with the net result that silver was recovered from each of the baths at almost similar rates, despite the difference in current.

In low current density electrolysis, the bath becomes progressively more acid as electrolysis continues, so plating can be carried out without much attention to pH values if the film is rinsed before it enters the fixing bath. In cases where the film is not rinsed, the carried-over developer will cause the pH of the fixing bath to rise, with the result that silver plating will eventually be affected. To prevent this, the pH of the bath should be maintained by the periodic addition of acetic acid.

(d) *Effect of Halides on Electrolysis.* Since silver enters the fixing bath as one or more of the silver halides (chloride, bromide, and iodide), the halide ion concentration will slowly increase during exhaustion of the bath, even though the silver is being removed. Hickman found that bromide concentration lowered the maximum tolerable current density value slightly up to a concentration of about 35 grams per liter. Beyond this point brown-plating occurred unless current density were reduced. Despite the brown-plating, however, continued electrolysis at the same or only slightly lower current density did not cause complete sulfiding and ruining of plate, over the range of 35 to 80 grams of potassium bromide per liter.

In the case of exhaustion of an unreplenished bath, the halide build-up will depend on the type of emulsion. The most silver-rich emulsions, such as industrial no-screen x-ray films, will raise the bromide (as potassium bromide) concentration to 30 to 40 grams by the end of the useful life of the bath. Even this build-up has not been found to affect the quality of silver plating in tests with low current density apparatus. With other types

of emulsions, such as amateur roll films, the halide build-up is considerably less. It is doubtful that bromide concentration would ever build up to harmful concentrations in systems using the low current density apparatus.

(e) *Effect of Carried-Over Processing Solutions on Electrolysis.* During processing, the fixing bath is continually being diluted and contaminated with solution carried over from previous baths. The effect of pH on electrolysis has already been discussed. The developing agents carried into the bath, while having no visible effect on the quality of the silver plate, are oxidized and the oxidation products color the fixing bath. This discoloration, which has also been noted by C. J. Sharpe,<sup>16</sup> can become quite intense towards the end of the useful life of the bath and the brown color formed is sometimes mistaken for the first stages of sulfiding. Inspection of the silver plate will determine which reaction is occurring.

The intensity of the color developed depends; in part, on the sulfite concentration of the bath, with high sulfite concentration tending to inhibit color formation. Other factors affecting the rate of color formation would include: (1) anodic current density, (2) the rate of carry-over of developing agents, (3) replenishment rate, and (4) degree of agitation. In one practical test in a 10-gallon fixing system, the transmission of the electrolyzed fixing bath at the end of its useful life was 10 percent (1 cu. cm. to 450 mμ light) or about the color of weak coffee, but the fixing properties of the bath and the silver plate were not affected.

(f) *Sludge in the Fixing Bath.* In most fixing-bath systems, a quantity of insoluble material collects in the bath. These impurities generally consist of coagulated gelatin, some precipitated hardener, dust, and other impurities that have either fallen in the bath or have been carried in on the film. During electrolysis these impurities are attracted to the cathode and are eventually plated over with silver. This roughens the plate surface and eventually causes it to darken somewhat. This darkening, under normal conditions, does not become serious before the silver plate is heavy enough to be stripped from the electrodes.

When high agitation and high current densities are used, the problem becomes serious if this sludge is not continuously filtered from the bath. The roughened surface of the plate cannot be replenished efficiently with the silver-rich solution, so that sulfiding occurs.

In both cases the sludge can stop silver plating by "shorting-out" the cell unless it is properly designed. When insulating supports used to separate the anode and cathode plates are below the surface of the fixing bath, the sludge will deposit on them and eventually short-circuit the electrodes. The only solution to this is to clean the supports periodically, or design the unit so that none are necessary.

(g) *Fixing-Bath Formula Variations.* Throughout this discussion, fixing baths have been referred to only generally as sodium or ammonium hypo baths, in spite of the fact that there are a large variety of fixing-bath formulas, particularly of those containing sodium hypo. However, formula variations beyond the already discussed variations in type of hypo, sulfite content, and pH value did not significantly affect experimental results.

For example, the presence or absence of chrome or potassium alum hardening salts, boric acid, acetic acid,

and borates, in baths of equal sulfite content and pH value did not appreciably affect the quality of the silver plate or the various conditions necessary for satisfactory electrolysis of the bath. Most baths of the same general composition as the acid hardening Kodak Fixing Bath F-5, would require the same maximum current density for trouble-free electrolysis. Baths having lower sulfite concentration, such as Kodak F-10, or having a higher pH value, such as Kodak F-24, would either require somewhat lower maximum current densities, or much more careful control to maintain chemical composition throughout the use of the bath so as to insure continuous electrolysis free from sulfiding reactions.

### C. Composition of the Silver Plate Formed by Electrolysis of Fixing Baths

Figure seven shows the cathode of a silver recovery unit from which the silver is being stripped, while next to it is a sample of the silver plate obtained from a previous run. When the plate has attained a thickness of  $\frac{1}{8}$  inch, it can be stripped fairly easily. After the silver-plated cathode is removed from the bath, rinsed, and dried thoroughly, the silver begins to crack and peel. Flexing the plate and tapping it with a rubber mallet will serve to remove most of the silver. Any that remains can be scraped off fairly easily.



Fig. 7. The cathode shown is from a low current density cell operated in a 10-gallon x-ray fixing tank for 30 days. Dark streaks in the silver plate formed during drying. The silver plate is stripped by flexing the cathode and loosening the plate with a spatula. Silver plate shown at the right was obtained from a previous run.



Thinner plates are more difficult to strip and considerable scraping is necessary. Heating the plate over a gas flame is sometimes necessary to break it loose. Therefore, it is advisable, so long as plating is proceeding satisfactorily, to let the plate get as thick as possible before stripping it.

Analysis of the silver plate formed in low current density cells shows it to be 95-99 percent pure silver. The silver plate in the illustration contained 98.5 percent silver. Impurities are for the most part gelatin degradation products, a little hypo, and other fixing-bath salts that have been occluded during plating.

### III. PHOTOGRAPHIC PROPERTIES OF ELECTROLYZED FIXING BATHS

Up to this point we have been concerned primarily with the chemical changes occurring during electrolysis of a fixing bath and their effect on plating. The next consideration is how electrolysis affects the photographic properties of the fixing bath, as compared to the nonelectrolyzed bath.

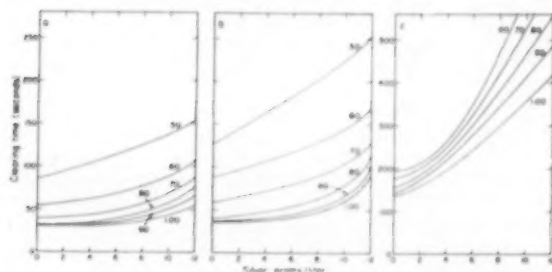


Fig. 8. The effect of silver concentration on clearing time of film fixed in an ammonium hypo fixing bath (Kodak Rapid Liquid Fixer) at various dilutions from full (1.00) strength to half-strength. A. Amateur roll film; B. High-speed panchromatic sheet film; C. No-screen industrial x-ray film. In terms of clearing time, the curves show that silver concentration up to 8 grams per liter and dilution up to 0.8 fresh strength has only a slight effect on the fixing properties with roll or sheet films. Successively higher dilutions, 0.7-0.5, have a much larger effect on increasing clearing time and to a greater extent than silver concentration over the same range of concentrations. The curves in Figure C for no-screen x-ray materials, however, demonstrate that at all dilutions silver concentration is the prominent factor affecting clearing time.

#### A. Changes Occurring During the Exhaustion of Unelectrolyzed Fixing Baths

1. *Silver Halide Concentration Build-Up.* Silver halide concentration gradually increases with exhaustion, and as it increases, the time necessary to clear an emulsion increases. Both the rate of build-up and the rate of increase in fixing time depend on the type of emulsion. Figures eight and nine show how the clearing time of various emulsions fixed in ammonium and sodium hypo fixing baths are affected by the silver concentration of the bath.

The increase in clearing time in these cases is primarily caused by the silver ion. The halides, except for iodide, have only a nominal effect in concentrations equivalent

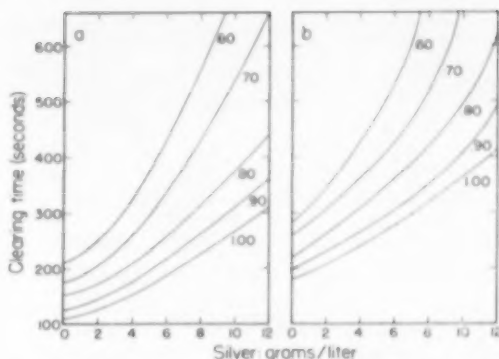


Fig. 9. The effect of silver concentration on clearing time of film fixed in a sodium hypo fixing bath (Kodak F-5) at various dilutions from full strength to 0.6 fresh strength. A. Amateur roll film; B. Industrial x-ray film (screen type). When compared to the similar curves in Figure 8, it is seen that in sodium hypo baths silver concentration has a more pronounced effect on clearing time. Particularly at the higher silver concentrations relatively small increments markedly increase the clearing time.

to the silver concentration. Iodide, on the other hand, can very markedly affect the clearing time in small concentrations. For example, the addition of iodide in a concentration of 2 mole percent of that of the silver concentration will increase the clearing time of film about 30 percent for baths containing 6 grams per liter of silver. However the iodide concentration rarely reaches this level.

*Dilution:* During processing, solution is continuously being carried over into the fixing bath by the film and, in turn, hypo-bearing solution is continuously being carried out. As a result, the bath becomes gradually less efficient, irrespective of the build-up of silver ion. Therefore, both silver halide build-up and dilution contribute to the exhaustion. Which of the two factors has the greatest effect on the bath depends on (1) the amount of carry-over per film, (2) the type of bath, and (3) the type of film.

In the case of ammonium hypo baths, dilution appears to be the primary factor causing exhaustion. Using the clearing time data given in Figures eight and nine and the Henn and Herzberger<sup>18</sup> equations for determining dilution rate in photographic processing systems, the curves shown in Figure ten A were derived for amateur roll-film types. These curves were based on carry-over rates prevailing with good draining (not more than 11 cc. per roll). Higher carry-over rates would bring the two curves even closer together.

With sodium hypo fixing baths under the same conditions of carry-over, silver build-up and dilution are both equally important under these minimum carry-over conditions, as shown by Figure eleven. However, these curves are representative of almost the optimum carry-over rates obtained in hand or semi-automatic processing. An increase in carry-over would once more bring the two curves together.

When silver-rich emulsions, such as some of the x-ray materials, are processed, the silver build-up is the im-

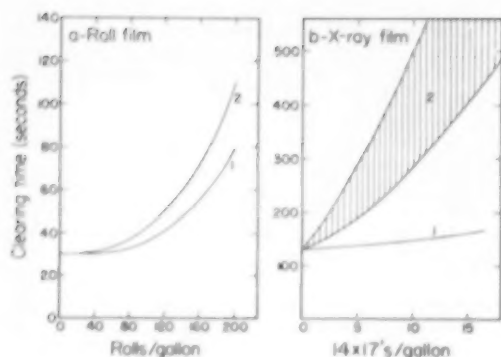


Fig. 10. Increase in clearing time with exhaustion of an ammonium hypo fixing bath (Kodak Rapid Liquid Fixer). No. 1 curves show the increase in clearing time due to dilution alone, while No. 2 curves show the increase in clearing time for both dilution and silver build-up. A. Amateur roll film; B. Industrial no-screen x-ray film. A range in No. 2 curve is given since the rate of silver build-up will depend on the type of emulsion and on the density and area of the image.

portant factor, as shown by the curves in Figure ten B for industrial no-screen x-ray film fixed in an ammonium hypo bath. This represents the extreme case. Most materials would produce curves more similar to those in Figures ten A or eleven.

2. *Effect of Replenishment on Fixing-Bath Properties.* The discussion in the preceding paragraphs relates to unreplenished fixing-bath systems in which the photographic properties of the bath change continuously. When the system is replenished either at periodic intervals or by continuous addition of fresh fixing-bath mixture, the composition of the fixing bath eventually reaches an equilibrium point. In this case, as compared to the unreplenished system, the rate of silver build-up and rate of dilution are slower, with the result that the change in the clearing time is slower. The ultimate composition of the bath and the rate of increase of clearing time are determined by (1) the rate of replenishment, (2) the concentration of replenisher, and (3) the rate of carry-over. It should also be noted that during replenishment an amount of solution must overflow from the fixing tank equal in volume to the replenisher added.

The replenishment system is actually used for two purposes, namely: (1) it serves to extend the useful life of the fixing bath and result in a saving of chemicals, and (2) it is also used to keep silver concentrations at a low point that will insure good stability of the washed and dried material.

## B. Effect of Electrolysis on the Course of Fixing-Bath Exhaustion

From the foregoing discussion it is seen that lowering the silver concentration by electrolysis will, in some cases, alter the course of fixing-bath exhaustion. The magnitude of the effect depends on the type of bath and

the capacity of the unit to maintain minimum or slowly increasing silver concentration.

With an unreplenished system, when the capacity of the recovery unit is such that it recovers silver at an average daily rate 20 percent or less than that at which it enters the bath, the photographic properties will not be affected throughout the course of exhaustion so long as the conditions are maintained (proper current density, adequate sulfite and initial silver concentration) for good silver plating. The change in silver build-up rate caused by electrolysis is not great enough to have any appreciable effect. When the rate of silver recovery approaches the rate of input, the effects vary with the bath and the film as follows:

### 1. Ammonium Hypo Fixing Baths

(a) *Amateur and Professional Roll and Sheet Films.* Referring to Figure ten A, it is seen that dilution is the primary cause for increased clearing time with exhaustion, even at optimum low carry-over conditions. Removal of the silver would, at best, lower the rate at which clearing time increases to the extent of obtaining 20 percent longer exhaustion life. With the higher carry-over rate usually found in practice, this advantage is wiped out, even for the emulsions slightly richer in silver.

(b) *X-Ray Materials.* Figure ten B amply demonstrates that a substantial increase in exhaustion life is obtained by removing the silver from the bath when processing the silver-loaded industrial no-screen x-ray materials. Even under regular darkroom practice, tests have shown that clearing time could be kept down so that the life of the bath could be extended to three to four times normal with this type of film.

With other x-ray emulsions it is doubtful if the fixing-bath life could be consistently extended more than 20 percent.

### 2. Sodium Hypo Fixing Baths

(a) *Amateur and Professional Roll and Sheet Films.* Figure eleven indicates that sodium hypo baths are somewhat more sensitive to silver build-up than the ammonium baths, with the result that removal of the silver has a more noticeable effect on reducing the rate of increase in the clearing time during exhaustion. Under optimum conditions of low carry-over rate, as much as 40 to 50 percent increase in exhaustion life of the bath might be obtained.

(b) *X-Ray Materials.* Sodium hypo fixing baths for these materials are generally more concentrated than for other films since the x-ray emulsions are richer in silver. However, with the carry-over rates generally employed when processing these materials, dilution accounts for a considerable part of the exhaustion of the bath. With the no-screen materials, a substantial extension of exhaustion life can be obtained, but with the other types of emulsion, exhaustion life cannot be extended more than 40 to 50 percent at best.

(c) *Photographic Papers.* In single-bath systems, exhaustion of the fixing bath is determined almost wholly in terms of silver concentration. It has been long known that the stability of finished prints depends on the

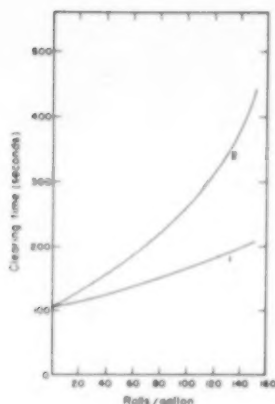


Fig. 11. Increase in clearing time with exhaustion of a sodium hypo fixing bath (Kodak F-5). Curve 1 shows increase in clearing time due to dilution alone, while Curve 2 shows increase in clearing time due to both dilution and silver build-up.

thoroughness with which the prints are washed free of hypo and particularly the silver thiosulfate complex.<sup>16</sup> This, in turn, depends on the silver concentration of the fixing bath in which the prints are processed. In practice, silver concentrations are often allowed to reach a value of 2 grams per liter, but when prints of good stability are desired, silver concentration is kept below 0.5 gram per liter.

It is seen, therefore, that the use of a silver recovery unit having a capacity to maintain low silver concentrations in a single-bath system would result in an extension of exhaustion life. In most cases this extension would amount to two times and could be as high as five times when the silver concentration is kept very low.

Over the past few years the long-recommended two-bath method of fixation<sup>16,17</sup> has been adopted by many commercial photofinishers, and most automatic paper-processing machines employ this system. The bulk of the silver in the emulsion is removed in the first bath, while the second "cleans out" the remainder. This has resulted in an over-all extension of fixing-bath life of two times.

In this case, dilution of the bath is the exhaustion-determining factor so that the use of silver recovery will not appreciably extend the life of the baths. Because silver concentration in the second bath of the system does not rise to more than 0.5-1.0 gram per liter during exhaustion and, in turn, depends on the silver build-up in the first bath, silver recovery is employed only in conjunction with the first bath. Under these conditions a maximum extension of fixing-bath life of 50 percent can be expected, at best.

3. *Use of Electrolysis in Replenished Systems.* Since a fixing-bath system is replenished for the purposes of lowering the rate of increase in clearing time caused by silver build-up and dilution, eliminating the silver by electrolysis of the bath should increase the life of the bath. Chemical cost may be cut in one of two ways: (1) by decreasing the rate of replenishment and using the bath for the normal length of time, or (2) using the same rate of replenishment and using the bath for a longer period.

In a few cases where silver build-up would be too rapid were it not for the dilution of the replenisher,

Table V

THE EFFECT OF ELECTROLYTIC SILVER RECOVERY OF FIXING BATHS ON LOWERING RESIDUAL SILVER AND HYPO IN PROCESSED PRINTS\*

	With Silver Recovery	Without Silver Recovery
Average silver concentration in fixing bath	0.76 gram per liter	2-4 grams per liter
Residual silver content in prints	0.003 mg. per sq. in.	0.007 mg. per sq. in.
Residual hypo ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) content in prints	0.06 mg. per sq. in.	0.120 mg. per sq. in.

\* In single-bath fixing system.

silver recovery might also allow concentration of the replenisher and a further reduction in replenishment rate.

In all cases, however, approximately the same proportional increases in fixing-bath efficiency, if any, would be afforded by the use of silver recovery as in the corresponding unreplenished systems.

There have been instances where electrolytic silver recovery has been installed in a fixing system and a change in the mode of replenishment has been made at the same time, the resulting increase in fixing-bath efficiency being mistakenly attributed wholly to the use of the electrolytic silver recovery. A common case is the one in which solid chemicals are used to replenish the bath in contrast to a liquid replenisher. This method of replenishment in itself is more efficient, although less convenient, than liquid replenishment since it reduces overflow losses, but even without silver recovery, a change to this system would result in more efficient use of the bath. It must be emphasized that when calculating gains in efficiency due to silver recovery, they must be based on the former use of the most efficient unelectrolyzed system.

4. *Effect of Electrolytic Silver Recovery on Stability of the Processed Materials.* It has already been pointed out that prints fixed in baths low in silver are washed more efficiently and, in turn, will have a higher degree of stability to staining and fading on storage. This may also be extended to film stability, although the maximum limits of retained hypo and silver complex are less critical. Since efficient silver recovery will maintain low silver concentrations, the result will be more easily washed, and more stable, photographic materials.

This is readily demonstrated by the following example: An experimental silver recovery unit was used to recover silver from a print-fixing bath and over a period of several weeks silver concentration was kept at an average level of 0.76 gram per liter. Normally silver concentration in this bath ran 2 to 4 grams per liter. Using the data given by Henn and others,<sup>17</sup> print stability, as measured by residual silver and hypo concentration, would be much better when electrolysis was used, as shown in Table V.

When the two-bath system of fixation is used, it would be difficult to show any advantage in washing through the use of silver recovery. The silver concentrations in the second bath are low in the first place and, although

recovering silver from the first bath would lower it even farther, little or no change in residual silver and hypo in the print could be expected.

5. *Other Secondary Effects of Electrolysis on Photographic Properties of Fixing Baths.* The improvement in fixing-bath efficiencies resulting from electrolysis is limited by a number of secondary factors, as follows:

(a) *Halide Build-Up.* As already pointed out, chloride, bromide, and iodide concentrations in the fixing bath build up during electrolysis even though silver is removed. Although the halide ions do not appreciably affect clearing time during the normal exhaustion period, their effect, particularly of iodide, will become noticeable when exhaustion life of the bath is extended. High halide concentrations will tend to accentuate the effect that silver concentration has on clearing time and, in an exhausted bath, a sudden increase in silver concentration that is beyond the capacity of the recovery cell may rapidly increase clearing time to a dangerous value. This effect, combined with the plate-poisoning effect of high halide concentration mentioned, will tend to limit the extent to which exhaustion of a bath can be increased by electrolysis.

(b) *Build-Up of Anodic Oxidation Products.* Both the reduction of hypo concentration and the build-up of tetrathionate and other polythionates by anodic oxidation will tend to limit extension of normal exhaustion life, the reduction of hypo concentration by oxidation adding to the effect of dilution on clearing time. The precise effect of the polythionates is not known, although Hickman states that baths relatively high in concentration of these products must be discarded.

The build-up of colored anodic oxidation products of developing agents carried over into the fixing bath has no effect on the rate of fixation. However, the concentration of these products becomes quite high during the normal life of the bath, and, if the bath is extended by prolonged use, or replenishment rate reduced, the concentrations of these products may reach the stage where staining of the processed materials will result.

(c) *Effect of Electrolysis on Hardening Action.* Quantitative measurements have shown that the hardening properties of an electrolyzed fixing bath are essentially similar to those of an unelectrolyzed bath in which an equal amount of film has been processed. Actually, in one test, swelling and abrasion measurements showed that film processed in the electrolyzed bath was somewhat harder due probably to the 0.3 unit drop in pH caused by electrolysis.

These results were confirmed qualitatively throughout the course of this investigation, no noticeable changes in hardening properties having been observed in practice when the various types of fixing baths were electrolyzed.

This section on photographic properties has been dealt with in some detail in the hope of rectifying some misconceptions concerning the degree to which fixing-bath efficiency can be increased by the use of electrolytic silver recovery. To summarize:

1. Electrolytic removal of silver from the fixing bath does not automatically extend the exhaustion life. The efficiency of many systems depends on the rate of dilution of the bath by carry-over which electrolysis cannot possibly affect.

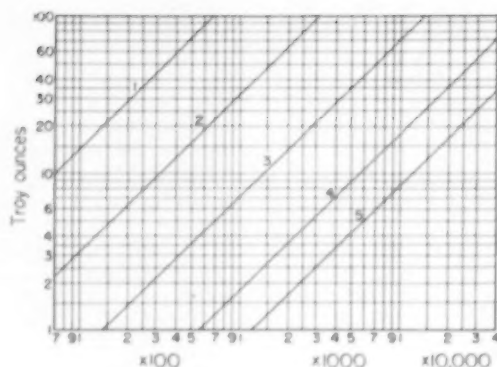


Fig. 12. Potentially recoverable silver from various photographic materials.

1-2. X-ray materials, 14- × 17-inch films. Curve 1 represents the maximum silver available from lightly exposed no-screen medical and industrial materials. If exposure is heavy, use one-half the figure obtained. Curve 2 is for medical and industrial materials used with fluorescent screens.

3. Amateur roll film (number of rolls) or 8- × 10-inch amateur and professional sheet films.

4. 8- × 10-inch sheets of photographic contact printing or enlarging papers. For negative line copy on projection papers, value should be decreased 50 percent; for positive line copy, value should be increased 50 percent.

5. Feet of 3½-inch paper for continuous print processors.

Note: To convert figures to grams, multiply by 30.

2. In general, efficiency of a fixing system cannot be increased more than 40 percent, at the most, and in many cases, little or no increase will be possible. In the special cases when silver-rich emulsions are being processed or low silver concentrations are required, electrolysis can increase fixing-bath efficiency two to five times.

3. Extending the fixing bath much beyond its normal exhaustion life through electrolytic silver recovery can involve some risk since changes in concentrations of the bath become much more critical as the end of the bath's useful life is approached. Furthermore, the build-up of reaction products of both electrolysis and fixation begin to have a detrimental effect.

When new replenishment systems are instituted concurrently with electrolytic silver recovery, careful analysis should be made to determine how much efficiency was due to each of the changes.

#### IV. THE ECONOMICS OF ELECTROLYTIC SILVER RECOVERY<sup>18</sup>

Large silver recovery cells have been in successful operation for many years and their economic value has been proved. However, it has been found necessary to operate them at nearly full capacity to realize an adequate profit, with the result that they have been employed mainly in the motion-picture processing laboratories and a few very large photographic establishments.

The more recent low current density units have been in use for a relatively short time and little pertinent data are available as to the financial success of their operation. The larger units, such as the Purhypo installation in



England, have been in use for the longest time and their continued use suggests satisfaction with their financial return. However, the various smaller units, which are generally sold outright, have been available in quantity for only a year or two. Therefore, in making the decision as to the advisability of employing small-scale silver recovery, a number of factors should be considered.

#### A. Potentially Recoverable Silver

Enough silver from the fixed materials should be available to operate the unit at full capacity. Figure twelve gives the silver yield that can be expected from fixing various types of photographic materials.

#### B. Efficiency

If the unit is to be used in a system where it may be possible to extend the exhaustion life of the bath, it must be capable of recovering silver at a rate somewhere near that at which it enters the bath; otherwise silver concentration will gradually build up and will also vary widely from the start to finish of a day's processing run. Under these conditions the possible increase in fixing-bath efficiency will not be realized.

#### C. Fixed Costs

From the gross return realized on the sale of the recovered silver from a year's run a number of fixed costs must be subtracted. These include:

- (a) Cost of the unit.
- (b) Cost of installation. The smallest units are designed to be placed directly in the fixing tank, with the power supply mounted nearby. Installation costs in this case are negligible. However, with other units, it is necessary to mount them outside of the fixing tank in a separate tank, either because they will be in the way when processing, or they are just too large. In this case, installation cost will include plumbing, mounting, separate tanks, if necessary, and the cost of a recirculating pump.
- (c) Operating and maintenance costs. The cost of power to operate the units themselves is negligible since most of the small low current density units are not rated at more than 10 watts. However, the operation of the recirculating pump, if necessary, may run up a significant cost. There is also the added cost of repairs, and the replacement of worn parts.
- (d) Handling and refining charges. The manufacturers of one recovery unit have an arrangement with a silver refiner who will accept all silver produced by these particular electrolytic recovery units. There are charges for packing, mailing, and insurance plus a refining charge between 4 and 5 cents per ounce of pure silver. If the silver is sold to another refiner, an assay charge of the order of 25 dollars would probably be added to the cost of disposing of the silver.

#### D. Net Profit and Labor

After fixed costs have been subtracted from the gross return, the remaining amount must adequately cover the labor spent in operating the unit.

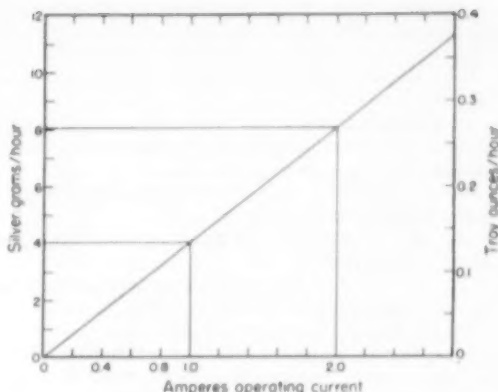


Fig. 13. Silver-plating rate for various values of cell-operating current.

The labor involved in operating the small units in terms of "man hours" per pound of silver recovered is at present difficult to determine but the units certainly require much less attention than the high current density units. However, their operation is still not a matter of setting them up and forgetting them. Time must be allowed to check and clean them periodically. A certain amount of continual control is necessary to balance their operation with the processing load. Also, account must be taken of time necessary to dismantle, strip off the silver, and reassemble the unit. Finally, there is the time required for disposing of the silver, and the book-keeping and correspondence involved.

The sum total of time spent on these various functions mounts up over a year's operation, and must be considered in any economic evaluation of the small-scale silver recovery process.

#### E. Chemical Savings

As already pointed out, the extent to which a silver recovery system will increase the useful life of the fixing bath depends on the particular fixing system employed and the type of materials processed. In some cases no chemical savings can be expected while, in others, a saving in chemicals of as much as 40 to 50 percent can add substantially to the net profit. However, under current methods of processing, it is doubtful that any appreciable savings in chemical cost can be expected in most cases.

The possibility still exists of improving this situation by controlling the carry-over rate. More complete draining or squeezing of the materials before they enter the fixing bath would reduce dilution rate considerably. If this was combined with silver recovery, it would definitely be possible to extend fixing-bath life and would result in substantial chemical savings.

Experience has yet to show how profitable small-scale electrolytic silver recovery can be. There are certainly cases where its use will be economically unsound, but to set a definite paper or film capacity as a minimum below which silver recovery would be unprofitable would involve a long listing of all the various systems combined with an equally long list of qualifications. Our hope is that this discussion will serve as a guide to

the prospective user of an electrolytic silver recovery system in reaching his own decision.

## V. SUMMARY

A. A successful long-term electrolysis of a given type of fixing bath in the absence of agitation requires the maintenance of the following:

1. A suitably low current density (0.05-0.40 ampere per square foot).
2. A minimum silver concentration (0.5 gram per liter or higher).
3. A minimum sulfite ion concentration (8 grams per liter of higher as sodium sulfite).
4. A reasonably constant pH value.
5. The absence of excessive contaminants.

B. Once these primary conditions have been met, electrolysis can be carried out in a given system until exhaustion of the bath results in the following:

1. Excessive concentrations of degradation products of gelatin or of silver halides causing sulfiding of the plate.
2. Excessive concentrations of products formed from the anodic oxidation of hypo and the developing agents carried over into the hypo.

C. Permissible current density levels vary with the type of fixing bath. In general:

1. Maximum current density levels are lower for sodium hypo baths than for ammonium hypo baths.
2. Maximum current density levels for alkaline baths of either type are lower than for acid baths.

D. Electrolysis will serve to extend the useful life of the fixing bath when:

1. Minimum carry-over rates prevail and silver concentration is the major factor causing exhaustion.
2. Silver-rich emulsions, such as x-ray materials, are being fixed and silver concentration rises rapidly with exhaustion.
3. Minimum silver concentrations are necessary to insure film or print storage stability.

E. The possible chemical savings that can be realized by extension of exhaustion life vary with the photographic material and the type of fixing bath as follows:

1. Approximately 20 percent for amateur and professional roll and sheet films and up to 400 percent for no-screen x-ray materials fixed in ammonium hypo fixers.
2. Approximately 40 percent for amateur and professional roll and sheet films fixed in sodium hypo fixers.
3. Approximately 200-500 percent with single-bath paper fixing systems.
4. Approximately 50 percent with two-bath paper fixing systems.

F. Electrolysis will have no really worth-while effect when:

1. Silver is not removed at a rate comparable to that at which it enters the bath.
2. Dilution of the bath due to carry-over of processing solutions is the major factor causing exhaustion.

G. The possible chemical savings in replenished system will be proportionally the same as those for un-replenished systems.

H. Silver recovery will be profitable if the gross re-

turn on the silver plus chemical savings adequately covers:

1. Cost of the recovery unit, of installation and of maintenance.
2. Handling, shipping, insurance, assay, and refining costs.
3. Cost of labor necessary to operate the unit and to strip and dispose of the unrecovered silver.

## VI. CONCLUSION

From the foregoing discussion it is apparent that the electrolytic silver recovery process is quite complex even when cells of the low current density type are used. From a chemical standpoint it is indeed complex, but the practice and application need not be difficult once a little insight has been obtained into the problems involved.

The fact that the available number of low current density silver recovery units is steadily increasing indicates a very definite interest on the part of photographers to prevent the continual loss of silver down the drain, and silver recovery by electrolytic means presents several advantages.

The first advantage, of course, is monetary. Although the number of dollars profit from a year's successful operation of a small-scale cell will never be particularly large, it will still represent an improvement in over-all efficiency of the processing plant.

Secondly, the amount of control that is necessary to operate the electrolytic units requires a closer than usual watch of the whole fixing system and will undoubtedly result in more efficient use of fixing chemicals, even beyond that made possible by electrolysis itself. Also, a well-operated electrolytic recovery system can result in producing a higher-grade product owing to more efficient washing and subsequent better stability than can be realized from processing materials in baths with a continually increasing silver concentration.

The main disadvantage of the process is that it requires extra time. The apparatus involved will take up space directly in the fixing tanks and hinder operations or, if an exterior unit is used, it may further crowd an already crowded darkroom. There is also risk involved in operating the unit if current densities near the maximum tolerable value are used. Accidental sulfiding of the fixing bath necessitates time-wasting shutdown and a loss of photographic materials and chemicals that could wipe out a good part of the profit which required some time to obtain. Only experience gained with the long-term use of the cells will determine the true practicality of low current density electrolytic silver recovery.

Further use of the process will also lead to improvements in design of the cells currently available. Since cells exterior to the machine are a necessity in many cases because of space limitations in the fixing tank, it may be possible to make them more efficient through the use of agitation.

Experiments with moderate air agitation<sup>12</sup> have demonstrated that lower minimum levels of silver concentration or higher operating current density can be tolerated. This would lessen the risk of sulfiding and result in more complete recovery of the available silver. If provision of this type of agitation could be made without greatly increasing the cost of the unit, it would

result in an appreciable advantage to the user both in efficiency and in ease of operation.

## VII. PRACTICAL RECOMMENDATIONS<sup>10</sup>

Manufacturer's instructions for operation of silver recovery units are usually fairly complete but the following suggestions may be of value.

### A. Choice of Silver Recovery Unit

A rough calculation of the average weekly input of silver to the fixing bath should be made and a unit chosen having a capacity to recover somewhere near this amount. If rate of input and recovery capacity are nearly equal, or the capacity of the unit is somewhat greater, careful control will be necessary in operating the unit but recovery will be effective and some savings in chemical cost will be realized.

If the capacity of the unit is well under the input, operation will require much less attention but there will be no chemical savings under any condition, nor will the benefits of improved photographic properties be realized.

A unit having variable control of current density is desirable, since this will make it possible to adjust the silver-plating rate up the silver input rate when it varies.

If the unit is mounted exterior to the fixing tank and a recirculating pump is employed, provision should be made for automatic shutdown of the cell if the pump stops. This prevents accidental sulfiding of solution in the recovery cell which can happen when recirculation in the system is stopped. A filter in the recirculating system is also desirable, since removal of any sludge that is formed would insure better long-term silver-plating.

A silver recovery unit should also be designed so that graphite or carbon is the only uninsulated positively charged material that will come in contact with the fixing solution. Some recent instances of cell breakdown have been found to be caused by corrosion of uninsulated metal brackets used to hold the graphite anodes in place and supply current to them. Corrosion of metal parts not in direct contact but in close proximity to the anodes has also occurred in a few cases. This can be prevented by suitably grounding the tank containing the recovery unit.

### B. Operation

1. *Silver Supply.* The instructions of the manufacturer of the unit usually specify the film-processing load that should be maintained to give an adequate supply of silver for the recovery unit. Generally this load is such that it will allow build-up in silver despite electrolysis. (Alternately the current density employed in the unit may be sufficiently low that sulfiding will not occur under any condition. However, it is not believed that any of the units available in this country employ such low current densities.)

If it is desired to operate more efficiently, silver concentration in the bath can be judged by the appearance of the silver plate. If the plate begins to brown appreciably, the silver concentration is low and the unit should either be shut off for a while or, if possible,

the current density reduced. If frequent checks of the plate condition and suitable adjustments of current are made, this method can prove quite efficient both from the standpoint of recovering a large percentage of the available silver and from the standpoint of extending the working life of the fixing bath, dilution rate allowing.

2. *Electrolysis of Baths When Not Processing Film.* Usually, the silver recovery unit is operated only when film is being processed. However, if the low capacity of the unit allows a continual build-up in silver concentration, it is possible to gain a little in efficiency by reducing the silver concentration of the bath during off hours. When and how long off-hour electrolysis can be made, can be determined by keeping a tally of the amount of film processed and making a few simple calculations.

Silver is plated at the rate of 4 grams per ampere-hour, ampere-hours being determined by multiplying plating current by 3600. Figure thirteen gives the silver-plating rate for various current values. By using Figure eleven, the total available silver for a given amount of film can be found and, allowing for a 50 percent loss of this amount due to carry-over during processing, the total silver in the bath available for plating can be determined. From these figures the possible extra hours of plating can be calculated as follows:

- Determine total available silver, using Figure ten, for a day's run.
- Divide this figure by 2.
- Divide this figure by the plating rate (see Figure eleven).

This result will give the total hours of electrolysis necessary to remove the silver from the fixing bath supplied by one day's run of film. For example:

- 1500 rolls of film will yield about 300 grams of silver to the fixing bath.
- Assuming 50 percent efficiency,  $\frac{300}{2} = 150$  grams of this silver can be recovered.

- At a plating rate of 6 grams per hour obtained by operating the recovery unit at 1.5 ampere, it will require  $\frac{150}{6} = 25$  hours of electrolysis to recover the silver from a day's run.

Therefore, it would be safe to operate the unit around the clock.

3. *Maintaining Sulfite Concentration.* Since the sulfite necessary to insure good plating is used up by electrolysis, carry-out, and dilution, it may be necessary to replenish the fixing bath with sodium sulfite at intervals. Table IV gives the conditions under which it will be necessary to replenish sulfite, and the replenishment rate.

4. *Maintaining Acid.* Since maximum tolerable plating current becomes lower as the bath loses acidity, the acidity of the bath should be maintained below a pH of 5.0 to insure good plating. (Even without silver recovery, acidity of the bath should be maintained to prevent loss of hardening action, staining of the film, and sludging in the fixer.) If an acid stop bath is used before the fixing bath, acidity of the fixing bath will be maintained. In its absence, however, periodic additions of acetic acid should be made. Henn and Crabtree<sup>20</sup> have described a suitable method of testing the acidity of various stop baths and fixing baths.

5. *Trouble-Shooting.* During operation of the silver recovery unit, times will occur when sulfiding or browning of the plate cannot be overcome by reducing current density or by shutting off the unit. In these cases, the silver concentration should be checked. The potassium iodide tests described by Henn and Crabtree<sup>20</sup> measure silver concentrations in the range of 0.5 to 1.0 gram per liter and will, therefore, indicate if the silver concentration has become dangerously low. If allowing the silver concentration to build up does not eliminate brown-plating, it is due either to low sulfite or high gelatin concentrations, particularly if this condition appears towards the end of the useful life of the bath. Good plating can be obtained in the former case by replenishing with sodium sulfite in an amount of 5 grams per liter (19 grams per gallon). In the latter case the addition of 1 gram of thiourea per 5 gallons of fixer will counteract the effect of excess gelatin.

If brown-plating persists, it would be advisable to discontinue electrolysis until the fixing bath is discarded and the system refilled with fresh fixing bath.

### C. Extending the Life of the Fixing Bath

The extent that fixing-bath life can be extended by electrolysis will depend on the judgment of the user. It is recommended that processing technique should not be changed when electrolysis is first introduced. Only after experience has been gained in its operation and when the changes in photographic properties resulting from electrolysis are known, should any modifications be made.

In replenished systems, for example, the same replenishment rate should be maintained in the first run. It may be found that the clearing time of the film near what would normally be the end of the run may still be low enough so that the bath can be used for a longer period of time before discarding. In this case, the replenishment rate might be cut slightly, say 10 percent, in the next run and the effect observed. Use of the testing methods described by Henn and Crabtree will be an aid to following exhaustion characteristics of the fixing bath. If this method of judicious experimentation is followed, any benefit in chemical savings that may exist can be realized without costly losses in chemicals and photographic materials.

### D. Tailing

It has long been the practice when employing high current density electrolysis to use a system called "tailing" to get more efficient silver recovery. This involves removing the bulk of the silver from solution with one cell operated at a high current density and removing the remaining silver by passing the solution through a cell operated at a lower current density.

A similar system can also be of use in low current density electrolysis, when using cells exterior to the machine. Silver builds up rapidly during processing, and to slow this rate of build-up, the operation of two separate cells in series will prove useful. The first cell which receives the silver-rich solution can be set at a somewhat higher current density than the second, to remove the bulk of the silver. The second operates at

the usual current density<sup>21</sup> and acts as the stripper. In off-hours the first cell is shut down and the second cell is used to catch up on any build-up in silver concentration that has occurred.

Theoretically, this could be repeated with additional cells, each operated at a lower current density in the series, and thus keep silver at a very low level. In practice, however, the rate at which these additional cells recover silver is not large enough to cover the cost of installing and operating them.

The main object of such a system is to minimize the losses in silver carried out during processing and in the overflow caused by replenishment. A refinement in the tailing system in connection with a replenished fixing-bath system would be to pass the overflow solution continuously through one of the displacement silver recovery units, such as the Gopher Unit. This would at least cut the losses of silver in the overflow.

In concluding these recommendations, the authors would like to add a note of caution. Low current density electrolytic silver recovery, while much less critical than the high density system, still requires attention, as the foregoing discussion emphasizes. Particularly when electrolytic silver recovery is first installed, the operator should pay close attention to its operation until he finds out the operating characteristics in his own fixing-bath system. Extension of the operating life of the fixer or changes in replenishment rate should be made slowly, a little at a time, so that maximum efficiency will be obtained without costly losses. Once the best operating conditions have been found, care should be taken to see that they are continuously maintained. It is only in this way that effective use of electrolytic silver recovery can be made and result in a true profit to the user.

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## SIMULTANEOUS MULTIPLE DYE TRANSFER COLOR PRINTING

John O. Brostrup\*

MANY SCIENTIFIC, educational and commercial organizations have had need for a limited run of full color print reproductions of color transparencies. The high cost of color engravings has eliminated their use in many instances no matter how worthy the project.

This paper describes a system of reproducing several relatively small color prints simultaneously by the Eastman Kodak Dye Transfer process at a cost which compares favorably with short run letterpress or lithography. This system is practical for a run of about 300 reproductions of each illustration, a number which is sufficient for illustrating a printing of many scientific, research or educational papers.

In addition to the relatively favorable cost relationship to other forms of short run color reproduction, there is the great advantage of the higher quality standards of Dye Transfer printing. Continuous tone (detail is not broken up by a halftone screen) and the extended range of contrasts in the highlight areas are two vital considerations in scientific illustrations. Where faithful resolution of fine detail is required, as, for example, in photomicrography, Dye Transfer printing is most advantageous.

In April 1952 this laboratory was assigned the job of reproducing 300 copies each of 10 color transparencies of photomicrographs and gross medical illustrations. To produce 3000 reproductions in addition to the existing heavy work load in the color branch seemed economically and practically impossible under the normal transferring procedure of about ten minutes per print.

The range of size changes of the ten originals was from same size to eighteen times magnification. It would

have been relatively simple to make the best possible duplicate color transparency to the proper size, combine these duplicates into a unit and then mask and separate from this combination. For ultimate quality it is desirable to work directly from original color transparencies. This paper describes such a system, altering sizes and combining these into page groups on a single set of matrices.

In brief, the ten original transparencies were grouped into pages of two, three, and five illustrations and two of these pages were on one set of matrices, making a total of three sets of matrices carrying four, six and ten illustrations respectively. Thus, instead of 3000 transfers the job was done with 450 transfers.

The procedure was essentially as follows. After the usual highlight and two principal masks and color separation negatives were made, the separation negatives were mounted on opaque acetate sheets in register and punched. It is at this point that this system departs from routine procedure. A specially constructed register punch board makes it possible to register several sets of color separation negatives simultaneously. There are also other modifications from the normal masking, separation and Dye Transfer techniques.

While the system described in this paper has worked very successfully in our laboratories, the specifications concerning metering, exposure and development times applied to the transparencies at hand and would not necessarily apply to other transparencies and other working conditions. Density and contrast of original color transparencies, variations in materials, solutions and individual handling are variables which have to be considered. The data regarding metering, exposure and development times will serve as a guide from which others may determine the conditions most suitable to their peculiar transparencies, materials and operating techniques.

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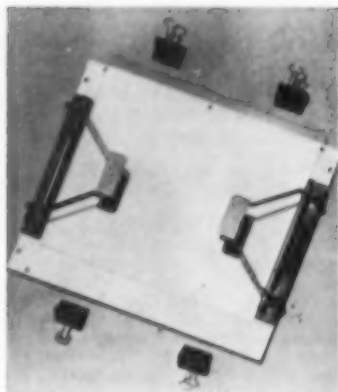


Fig. 1. Double end register punch board with opal glass bottom for use over a light table.

### Equipment Required

In addition to the equipment and supplies normal to routine dye transfer printing the following equipment is required.

1. A specially constructed double-end register punch board. (Figure one). This board has two Eastman Kodak Matrix Film Punches, one on each end. It has an opal glass bottom and during registration of the matrices the board may be placed on a light table.

2. A light table of average brightness with a built-in #2 Photoflood bulb on an independent foot switch.

3. A densitometer, although not absolutely mandatory in routine Dye Transfer printing, is essential to this system. The Kodak Color Densitometer Model 1 is satisfactory. This laboratory uses the Ansco Model 12 Densitometer. Over the densitometer are placed two Kodak 10" X 10" Color Transparency Viewers. The top one, pointing downwards, illuminates the Dye Transfer print with light of the same quality as that on transparency on the lower viewer.

4. A Model 200M Photovolt Light Meter for standardizing exposure conditions of masks, separation negatives and matrices. The Model 200M Photovolt has a sensitivity of 2 foot candles when meter reads 100 on HIGH. The HIGH scale is 10 X the LOW scale, thus 10 on LOW equals 100 on HIGH. All readings are taken with the base of the cell on the film plane or at the film plane plus glass.

5. A Model TM-8 Lectra-Laboratories Electronic Timer for making exposures with 1/10 second accuracy.

6. A Model V-1M Variac Voltage Regulator Transformer with voltmeter. All exposing conditions for every operation were standardized at 120 Volts with exposing lamp ON.

7. An 8" X 10" contact printing frame.

8. An 8" X 10" piece of thinly flashed opal glass, free from striations, bubbles or specks.

9. An 8" X 10" piece of flawless glass. Glass of this type with ground and polished edges may be obtained from J. G. Saltzman, Inc., 480 Lexington Avenue, New York, N. Y.

The items listed in 4 to 10 are shown in Figure two. The Goerz Apochromat Artar coated lenses have been

found most satisfactory for making enlarged separation negatives.

When the enlarger is used as a light source only, as for making grey scales, masks, separation negatives and matrices by contact, it is racked up fairly high and lamp and lens adjusted to give as even illumination at the easel as possible. It has also been found necessary to place a piece of thinly flashed opal glass in front of the lens. A cone of black paper should be placed between the lens and opal glass to prevent stray light from reaching the easel. When separation negatives are made by projection, of course the opal glass is removed, but the paper cone and filter remain.

### Preliminary Considerations

Only color transparencies of the best quality should be selected for Dye Transfer printing. For medical subjects color transparencies of fresh gross clinical specimens are preferred since fixation removes or alters natural coloration. In general, formalin solution removes or greatly alters practically all natural color; Kaiserling's solution preserves some color in selected specimens, and grain alcohol fixation preserves considerable color in certain tissues. The preservation of color and other qualities of animal or vegetable tissue is a complex subject. It is thoroughly discussed by Mallory in *Pathological Techniques*.<sup>1</sup>

Color transparencies of fresh clinical specimens are often unavailable. Dye Transfer prints have to be made frequently from first rate color transparencies of fixed specimens, giving consideration at all stages to altering the technique so that the final print will be corrected in the direction of the color of the fresh specimen.

Whenever possible, the closest liaison should be maintained between the laboratories preparing sections for color photomicrographs and the photographic laboratory. Close cooperation will assure the best sectioning and staining techniques and also the best color correction and resolution of detail.

For all color transparencies this simple rule should obtain, "to make a good color print from a transparency, start with a good original."



Fig. 2. Model 200M Photovolt in use. Opal glass in front of lens and position of filters. Also shown are the timer and voltage control.

After the color transparencies have been selected the next consideration is to determine layout arrangement and final size requirements. Usually this will follow the requirements of an accompanying text. The pages in this text were 6" X 9", including a 1 inch margin at the left for binding.

The page or pages should be accurately laid out on bond paper. As noted earlier, size changes ranged up to eighteen times magnification. Since size changes present no obstacle, cropping should be judicious. The illustrations were "bled" to the edges of the page and separation between illustrations was 1/8 inch.

### Preparation of Transparencies

If possible, the original transparency should be cut to a size only slightly larger than the area to be included in the final reproduction. This refers only to subject matter, as enlarging or reduction will be accomplished at a later stage. Thirty-five millimeter transparencies should not be cut.

The purpose of trimming off unwanted subject matter of original color transparencies is to locate register marks and step tablet grey scale as close to the final image area as possible. These register marks should have about 25 per cent grey fogged density to prevent their over-exposure on the separation negatives.

The procedure for making register marks and attaching them and the grey scale to the color transparency is described on pages 17 to 20 of Eastman's "Masking Color Transparencies for Photomechanical Reproduction."<sup>7</sup> Usually two register marks at opposite corners are sufficient. The grey scale should be located on an edge which will not be trimmed away later when separation negatives are mounted in close proximity. Typical positions for register marks and grey scales are shown in Figure three.

The Kodak 21 Step Tablet No. 2 has a density range of 0.0 to 3.0 and is very satisfactory for sheet film color transparencies. Grey scales of 15 steps ranging from 0.2 to 2.5 density are made in the laboratory. Three sizes of scales will cover all needs, scale lengths being 3.0, 7.0 and 15.0 millimeters. These scales are easily made on Eastman Fine Grain Positive sheet film. Exposures of steps will range from about 0.7 second to 80.0 seconds with a Photovolt reading of 5 on HIGH at the film plane.

For even development, each sheet of Fine Grain Positive Film is processed individually in a tray, with constant agitation throughout. The procedure is as follows: (a) rinse in water 1 minute; (b) develop in D-72 diluted 1 to 3, 4 minutes at 68 F.; (c) short stop 1 minute; (d) fresh hypo 4 minutes; (e) wash 20 minutes; (f) rinse in Photo-Flo solution and dry. One hundred cubic centimeters of 0.5 per cent Benzotriazole solution should be added to each gallon of stock developer, when D-72 developer is used for making grey scales.

The ideal grey scale should have densities ranging from 0.2 to 2.5 in uniform steps so that when it is graphed it will form a straight line. The procedure for graphing a grey scale is described in "Color Separation and Masking."<sup>8</sup> We have found that it is unnecessary to have steps below 0.2 in density on the grey scale as that is beyond the range of satisfactory highlight detail.

After attaching grey scale and register marks to the transparency, densitometric readings are made of the ex-

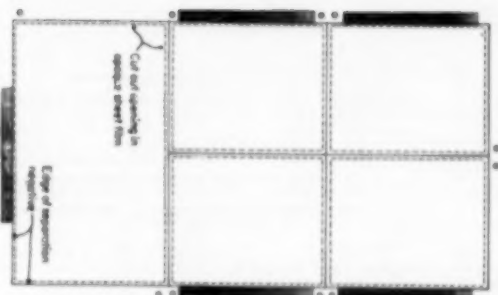


Fig. 3. Location of registration marks and grey scales for a five illustration page layout.

tremes in density, non-specular highlight and deepest shadow in which it is desired to hold detail. Next, indicator marks are placed on the two steps on the grey scale that most nearly match the two extremes in density of the transparency. On the step matching the highlight density a mark is drawn with pen and India ink. On the step matching the shadow density a mark is scratched with an etching knife.

The densities of the color transparency and the matching densities of the grey scale are now recorded on Kodak Color Separation Record Sheets. The recording of data of every step throughout the production of masks, separation negatives and matrices is essential to success. Experience will dictate alterations of density and contrasts. Without standardization of operating procedures and recording of data, the necessary modification of exposure and development times cannot be accurately determined.

Throughout the procedure described, and as generally employed in the graphic arts industry, all films are code notched on the edge adjoining the normal film identification notch. Standard code notching is as follows: NO NOTCH, red filter principal mask, red filter separation negative, cyan printer matrix; ONE NOTCH, green filter principal mask, green filter separation negative, magenta printer matrix; TWO NOTCHES, blue filter separation negative, yellow printer matrix. The edge notcher for motion picture film found in most photographic supply stores is ideal for code notching.

### Highlight Masks

The general density and contrast requirements of highlight and principal masks described in "Color Separation and Masking," Eastman Kodak Company,<sup>8</sup> apply to this system. The manner of producing these masks, however, has been somewhat altered.

For all masks the enlarger is used as a light source. In front of the lens is placed a piece of thinly flashed opal glass (Figure two). Instead of a Kodapak Diffusion Sheet, a second piece of thinly flashed opal glass is used as a diffusion medium but not in the same position as the Kodapak.

The orientation of opal glass, color transparency, Highlight Masking Film and black backing paper during exposure of the highlight mask is shown in Figure four. A backing sheet of matt surfaced black paper prevents an exposure of halation type when highlight



Fig. 4. Orientation of opal glass in printing frame, color transparency, Highlight Masking Film and black backing paper during exposure of highlight mask.

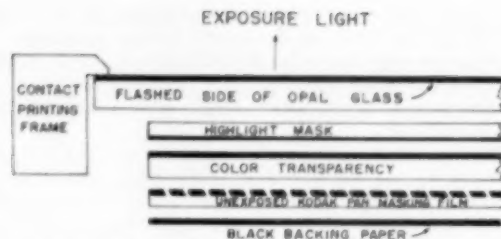


Fig. 5. Orientation of opal glass, highlight mask, color transparency, Pan Masking Film and black backing paper during exposure of principal mask.

and principal masks are made. The emulsion of the Highlight Masking Film is placed in contact with the emulsion of the color transparency and normally would be considered a sharp mask. The opal glass, however, has a diffusive influence that makes for ease of registration and eliminates "edge effect" in sharp-edged high contrast areas even with very great enlargements from 35mm originals.

Metering for highlight masks is standardized at 20 on HIGH on the Photovolt Model 200M Meter. Exposures may vary widely, depending on the density of the diffuse highlight area of the original color transparency. Experience indicates exposure times in the range of 3 to 15 seconds. Development is in Highlight Masking Film Developer and is never less than  $3\frac{1}{2}$  or more than  $4\frac{1}{2}$  minutes, with constant agitation, in a tray at 68 F. A small volume of fresh developer is used for each sheet of film.

All masks are fixed, washed, rinsed in Photo-Flo Solution and dried at room temperature in the shortest possible safe time to minimize size changes and consequent poor registration. Since the masks need not last indefinitely they should not be washed for more than 10 minutes.

The highlight mask is now registered on the emulsion side of the color transparency. After the highlight mask has been registered on 35mm color transparencies, it is helpful to scratch the emulsion of the highlight mask with a needle, running it around the inside edge of two opposite sprocket holes. After the principal masks are made, the resulting exposed lines will aid greatly in registration of the principal mask to the color transparency.

### Principal Masks

Two principal masks are made through the #29 and #61 filters, respectively. Orientation of opal glass, highlight mask, color transparency, Kodak Pan Masking Film and black backing paper during exposure of the principal mask is shown in Figure five.

Metering for principal mask exposure is standardized at 20 on HIGH, WITHOUT FILTER. Exposures will vary between 8 and 40 seconds for the mask from the #29 filter. The exposure ratio of 2 to 3 is always maintained between the #29 and #61 filters, thus typical average exposures are 20 seconds for the #29 filter and 30 seconds for the #61 filter.

Development is in DK-50 diluted 1 to 4, in tray at 68 F. from  $3\frac{1}{2}$  to  $4\frac{1}{2}$  minutes. Rinse, fix, wash for 10 minutes and rinse in Photo-Flo Solution before drying.

The principal masks are registered individually on the emulsion side of the color transparency.

### Separation Negatives

Separation negatives are made by contact or projection. The set of negatives must be made to the size of the desired Dye Transfer print, as all matrices by this system must be exposed in contact with the separation negatives.

The orientation of glass, principal mask, color transparency and separation negative film during exposure of separation negatives by contact is shown in Figure six. The orientation of glass, principal mask, color transparency and separation negative film during exposure of separation negatives by projection is shown in Figure seven. When separation negatives are exposed by projection, the color transparency and principal mask must be held in good contact between two pieces of flawless clear glass. The separation negative film may be held in position in a cut film holder. If a cut film holder is used, the same side of a single holder should be used and a rabbit cut in the mounting board to accommodate the light trap.

Metering for separation negatives on Kodak Super-XX Film is standardized at 5 on LOW WITHOUT FILTER for gross specimens (all average subject material) and 10 on HIGH WITHOUT FILTER for photomicrographs.

At this point special consideration must be given the printing by contact of all separations that will be grouped on a single set of matrices. Since there is no possibility of selectively altering the development contrast between different illustrations on a set of matrices, exposure and development times of the separation negatives must be such that the set of matrices can be developed in Matrix Developer diluted 1 to 2 and transferred using normal dyes.

These considerations would seem to be very limiting, but in practice they have improved the quality of all Dye Transfer printing, multiple and individual. When it is known in advance that separation negatives must be so adjusted that they will print ideally on Matrix Film developed in 1 to 2 developer, very good quality separation negatives will be achieved.

To produce ideal sets of color separation negatives from a wide range of original sources, an equally wide range of exposures, developers and developing times must be employed. The point to remember throughout the production of a set of color separation negatives is that the density range as marked off on the grey scale



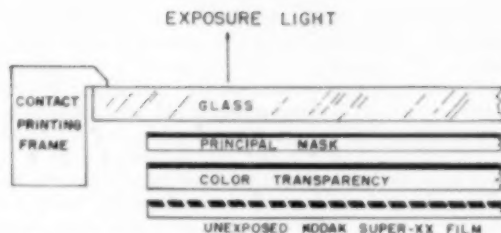


Fig. 6. Orientation of glass, principal mask, color transparency, and separation negative film during exposure of the separation negatives by contact.

must be compressed or expanded to fit the range of Matrix film developed in 1 to 2 developer. In practice, each individual illustration was masked, separated, matrices made and transferred *before* the separation negatives were combined into the page units. The test print matrices must be of the same emulsion number as the final matrices. With experience and, more importantly, with accurate standardization of metering, processing and recording of data, a technique can be developed to a point where the test prints from each individual illustration can be made with facility. Representative record sheets are shown in Figure twelve.

A guide to developers for color separation negatives on Kodak Super-XX Film for various conditions follows.

DK-60a, full strength: Masked color transparencies of photomicrographs. Photomicrographs are often very soft in contrast. This is the most vigorous developer needed for the lowest contrast, masked, photomicrographic color transparency.

DK-50, full strength; original separation negatives of charts, water color wash drawings, architectural renderings.

DK-50, diluted 1 to 1: Masked color transparencies of average subject material, scenes, portraits, and gross clinical specimens.

DK-50, diluted 1 to 2: Direct separation negatives of oil paintings of average contrast. Direct separation negatives of still life subjects, table top setups, flowers, fruits, merchandise etc.

DK-76, full strength: Direct separation negatives of oil paintings of high contrast. Cut developer times with this developer if necessary with some very high contrast oil paintings.

Even with this wide range of developers it may be necessary to adjust developing times.

### 35mm, 16mm and 8mm Originals

An alternate method of masking and separating small original color transparencies follows. The original color transparency with grey scale attached is securely mounted *emulsion side up* between glass in the negative carrier position of a rigid enlarger. For this method there must be absolutely no movement or vibration of enlarger, easel, or register board combination from start to finish. The original color transparency remains undisturbed throughout masking and separating.

Highlight Masking Film, Pan Masking Film and color separation negative films are all punched in the Kodak Matrix Film Punch *before exposure*. All exposures

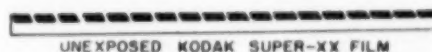
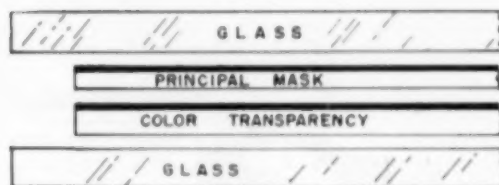


Fig. 7. Orientation of glass, principal mask, color transparency and separation negative film during exposure of the separation negatives by projection.

are made with films mounted *emulsion side up* on the register pins of a Kodak Small Register Board that has been securely fastened to the enlarger easel. The films are held flat with a piece of clear flawless glass.

After the highlight mask has been exposed and processed, it is mounted on top of the unexposed Pan Masking Film during exposure of the principal masks. Likewise, after the two principal masks have been exposed and processed, they are successively mounted on top of the unexposed color separation negative film during exposure of the separation negatives.

By this method, visual registration of masks is not required. It has proved very successful for masking and separating 35mm and smaller color transparencies.

### Backgrounds and Type

For certain gross medical specimens and other object color photographs it may be desirable to replace the background with one of a different color or neutral grey. The four gross specimens for this particular project had backgrounds of various colors. A neutral grey background was specified, as well as the addition of arrows, lettering and figure numbers.

First a high contrast negative is made from the unmasked color transparency. With proper selection of filters and use of either Kodak Kodalith Orthochromatic Film No. II or Kodalith Panchromatic Film developed in Kodalith Developer, high contrast separation between subject and background can usually be obtained (Figure eight). Rarely, the separation may be so slight as to require stepping up by making a contact diapositive and a contact negative from this diapositive. The negative should have opaque black areas and completely transparent open areas.

After a satisfactory high contrast negative is obtained it is opaqued to eliminate pin holes.

Next, an enlarged, contact, or reduced diapositive is made in exactly the same ratio as the color separation negatives, that is, if the color separation negatives were made by projection, the Kodalith diapositive must be

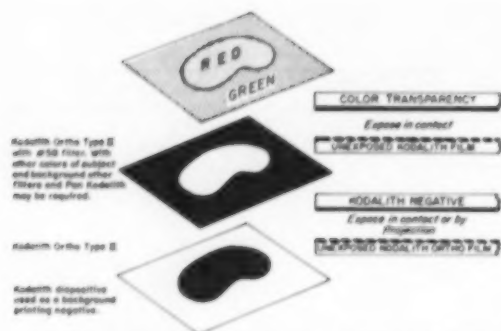


Fig. 8. Steps in the production of gray background printer negative from originals having colored or distracting backgrounds.

made at exactly the same enlarger setting. Negatives for arrows, lettering and figure numbers are also made on Kodalith film from standard type sources. The registration and use of these films are explained later.

### Method of Registration

Since more than one color illustration is required to be in register at a time on a set of matrices, all negatives for each illustration on a single page must be in register with others for the same illustration as well as symmetrically in register with all others. In letterpress and lithography there are accurate machines and methods to accomplish this multiple registration, but to our knowledge no equipment for this purpose and adaptable to the Dye Transfer process is available. The method of registration using the special double-end register punch board described in the section on equipment follows.

The sets of color separation negatives are mounted on sheets of opaque sheet film. An excellent film for this purpose is flash exposed and processed x-ray film. This film is especially suitable because it has an emulsion on each side and gives a completely opaque rigid support for the negatives.

Sheets of opaque film are securely thumb tacked to a drawing board, while firm pressure is exerted on a sheet of  $\frac{1}{4}$  inch plastic placed on top to hold all sheets perfectly flat. Openings are then cut out to proper size as predetermined by layout (Figure three). These openings must be accurately and uniformly cut with a steel straight edge and single edged razor blade or sharp knife. Three sheets of film are needed for the three sets of separation negatives and if a grey background and lettering are to be used an additional sheet of film for each is necessary. Small, square openings are also cut for the location of the register marks.

At this time an exposure template with trap door openings should be made (Figure nine). The openings are to enable individual exposures for every separation negative for each illustration. The edges of the doors are centered on the divisions between illustrations and have Scotch taped hinges.

Next, a single sheet of cut out film is mounted on the special register punch board, which is placed on top of the light table. One edge of this film is placed under the punch but is drawn out about  $\frac{1}{8}$  inch to facilitate

future registration of other sheets. At this stage in registering the negatives the second punch is not required and is removed. The edges are securely Scotch taped to the register punch board. All of the #61 filter negatives are now located *emulsion side up* on the opaque cut out film and edges are secured with DuPont cement.

A second sheet of cut out film is mounted on top of this combination. Edges of the openings are accurately registered with the bottom sheet by using a 5X magnifier. When these openings are perfectly registered the top sheet of film is Scotch taped to the register punch board. The top sheet of cut out opaque film should be Scotch taped in such a manner that it can be easily removed without disturbing the lower sheet with its mounted #61 filter negatives. The pieces of Scotch tape should not be superimposed on those holding the lower combination.

The #29 filter negatives are now individually registered over the appropriate #61 filter negatives, using the register marks. When critical registration is being done, the films are placed in as near perfect registration as possible using ordinary light table illumination. For the final "zeroing in check" the Photoflood is turned on by foot switch. The Photoflood should be on for the shortest practicable time as it generates considerable heat which might affect registration.

After all #29 filter negatives are registered and secured with DuPont cement, a piece of 1/4 inch plate glass is placed on top of the two combinations and held down firmly while the two pieces of opaque mounting film are punched.

After simultaneously punching the #61 filter combination and the #29 filter combination, the #29 filter combination (top) is removed. Care must be taken that the #61 filter combination remains firmly secured to the register punch board and is not disturbed until all combinations have been registered and punched.

Next, another sheet of cut out opaque film is registered and secured over the #61 filter combination. The #49 filter negatives are now registered and secured to the mounting film in the same manner as the #29 filter negatives. Again the glass is held in place over the two combinations while the film is punched. The #49 filter

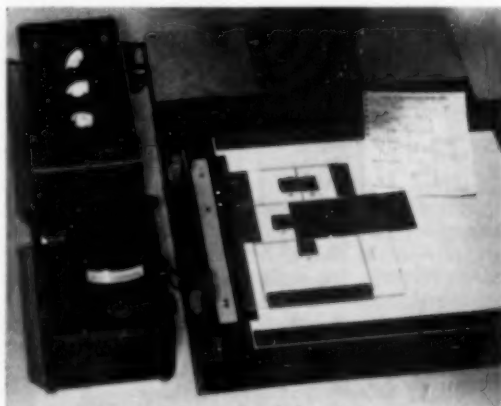


Fig. 9. Exposure template in use under enlarger light source when contact exposing the separation negatives.

combination is now removed without disturbing the #61 filter combination. After the separation negatives have been registered, the register marks are covered with black Scotch tape.

If grey background negatives or typed lettering negatives are involved, they are similarly registered on sheets of cut out opaque films and punched in register with the #61 filter combination.

One other item remains to be registered onto the #61 filter combination: the template with trap door openings.

After all combinations of separation negatives, background lettering and negatives and exposure template have been registered and punched, the #61 filter combination is removed from the register punch board.

We now have three or more combination sets of separation or other negatives which are not only in perfect register individually for each illustration but are symmetrically in register with all others.

### Preparation of Matrix Film

As many sheets of Matrix Film as are required for printing are now prepared for exposure. It will take three sheets for the cyan, magenta and yellow printers, plus one for the background and lettering. The grey background and all lettering, arrows and numbers can be printed on one sheet of Matrix Film.

The second punch is replaced on the double-end punch board, one having been removed during registration of the negatives. The following steps are carried on under very subdued Wratten #1A Safelight illumination.

The required number of sheets of Matrix Film *emulsion side up* and without any black separator papers between the sheets of film, are now placed in the double-end punch board. The Matrix Films should be oriented so that all film notches are in the same corner. A sheet of black separator paper is placed on the bottom and on the top of the Matrix Films. The width should be the same as that of the films, but the length should be 2 inches shorter than the films so that the black papers do not go into the narrow slot in which the film enters the punch.

A piece of 1/4 inch plastic is placed on the black paper and group of Matrix Films and is firmly held down with heavy binder clips. Both ends are now *punched simultaneously*. Two of the punched Matrix Films are left without code notching. One sheet is punched once along the adjoining edge near the regular film notch. The remaining sheet is punched twice along the adjoining edge near the regular film notch. All films are now replaced between black separator papers and boxed until ready for exposure.

### Exposure of Matrix Films

As will be seen from the data sheets under exposure of matrices, there is some variation in the exposure of each individual separation negative of each illustration. The selective exposures are accomplished by means of a template with trap door openings so that each separation negative is exposed individually (Figure nine).

The exposure of Matrix Film is carried on under very subdued Wratten #1A Safelight illumination. Starting with the #29 filter combination, a sheet of the pre-

punched *no code notched* Matrix film is placed on a large size register transfer board *emulsion side down*, and registered on the pins. Next, the separation filter combination is placed *emulsion side down* and registered on the pins. Next, a piece of thin grade "A" glass is placed on top of the film combination, and finally the exposure template is placed on top of the glass and registered on the pins.

Now by opening the trap doors of the template individual exposures as predetermined in the test runs are given each print. After exposing one end of the Matrix Film, the other end is placed on the register pins and the successive exposures made for that end.

If only one page of combined Dye Transfer illustrations is to be transferred at one time, the second Kodak Matrix Punch is not required and only one end of a set of matrices will be punched, exposed, processed and transferred. For this project it was essential to cut transferring operations to the minimum so two complete pages were on each set of matrices.

After the #29 filter combination has been exposed, successively the #61 and #49 combinations are exposed on the one code notch and two code notch Matrix Films. If grey backgrounds are required the backgrounds of the separation negatives are masked by registering the Kodak negatives on the combined acetates before exposure of the matrices. The grey background, arrows, lettering and figure numbers are all exposed on one sheet of Matrix Film.

### Developing Matrix Films

As mentioned earlier in the section on Separation Negatives all matrices for this system of Multiple Dye Transfer Printing must be developed in Matrix Film Developer diluted 1 to 2.

The stock solutions are kept in 1/2 gallon bottles in water baths maintained exactly at 68 F. The quantities of A and B solutions to be used for development are measured into beakers which are also kept in water baths at 68 F. The developing tray is also immersed in a larger tray holding water at 68 F. These considerations are very important, as the exposing and developing times and technique must be identical to the previous trial runs for each individual illustration.

Each sheet of Matrix Film is developed individually. Tests have shown that subjects with continuous tone backgrounds must be developed individually to avoid variations in color in different areas.

After developing in 1 to 2 developer for exactly 2 minutes the film is rinsed for 30 seconds in a tray of water at 68 F. It is then placed in a tray of Matrix Fixer for 2 minutes after which the room lights are turned on.

The following hot water wash has proved most satisfactory for a wide variety of critical Dye Transfer illustrations.

A timer is set for 2 1/2 minutes and immediately the Matrix Film is immersed *emulsion side up* in a tray of water at 120 F, rocking it gently for 30 seconds. The remaining 2 minutes the film is washed *emulsion side up* on the back of a white enamel tray of larger size than the Matrix Film. A gentle but adequate stream of water from a flexible length of soft latex hose is allowed to flow onto the emulsion. The end of the hose is covered loosely with eight layers of good quality lint-free cheese cloth secured with a rubber band (Figure ten).

Twice during the 2 minutes the film is held vertically by one corner and the tray and back of Matrix Film are rinsed to remove the back coating. The last 30 seconds the film remains on the back of the tray with water flowing and the edges of the Matrix Film are scraped clean with a finger nail to remove shreds of emulsion which might become embedded in the image area. Just before the  $2\frac{1}{2}$  minute washing time is over the film is again held vertically by one corner and rinsed on both sides under the hose.

At exactly  $2\frac{1}{2}$  minutes from start of the hot water wash the film is placed in a tray of water at 68 F for one minute then hung up to dry, wiping the *base side* only with a fine-pore viscose sponge. The usual precautions of hanging all matrices from the same corner should be observed.

While this hot water washing technique seems involved, it has been found the only one that will assure even tone coloring throughout a large background area of one continuous color. With a little practice the washing technique becomes second nature and can be easily and thoroughly accomplished in the allotted  $2\frac{1}{2}$  minutes. Matrix Films of all sizes including  $16\frac{1}{4} \times 21\frac{1}{4}$  are developed routinely by this method.

### Transferring the Matrices

The matrices are now ready for swelling, dyeing and transferring. The usual techniques are described in "Kodak Dye Transfer Process."<sup>4</sup> Since the test run for each illustration was dyed in normal dyes (no acetic acid added) the combined matrices are also given the same dye treatment.

Only one set of register punch holes is used at one time, that is, either the set on the ends having film notching or all of the opposite end, but they must not be used interchangeably.

Rarely it may be necessary to reregister the whole set of matrices on the register punch board to correct a slight discrepancy of registration. This can be accomplished by first dyeing, rinsing and drying the matrices. They can then be easily registered with the long edges of the matrices under the punch.

A rocking table has been found advantageous for speeding the dyeing of matrices (Figure eleven). If the matrices have been adequately swelled, they will be thoroughly dyed in 7 minutes. A 10 gallon storage tank with self closing spigot for one per cent acetic acid rinse is useful for continuous transferring operations. Acetic acid of  $1\frac{1}{2}$  per cent is used in the holding bath just before transfer. Naturally no highlight reducer or other contrast control techniques are permitted in this system of Multiple Dye Transfer printing unless *all* of the illustrations on a given set of matrices require such treatment. As described earlier, each illustration was test run for developing in 1 to 2 Matrix Film Developer, dyeing in normal dyes and transferring without using any control techniques. All control of contrast must be achieved at the stage of producing separation negatives. Control of density is accomplished at the stage of making Matrix exposures.

On production runs of Dye Transfer printing, accurate and regular replenishment of the dyes is essential for maintenance of color balance. The Fisher Scientific Company No. 3-842 10ml automatic burettes are ideal

for storage and dispensing of replenishment dyes (Figure eleven).

For ordinary Dye Transfer printing (not multiple) additional burettes for Highlight Reducer, 28 per cent Acetic Acid, and 5 per cent sodium acetate buffer solution are useful. When there is a black dye printer matrix one burette stores the replenisher for that dye.

The recommended replenishment schedule published with dyes is usually adhered to unless a predominance of one color necessitates some adjustment.

A working dye for the black matrix printer follows:

Cyan	630cc
Magenta	525cc
Yellow	805cc

A dye replenisher can be made up of stock dyes as follows:

Cyan	126cc
Magenta	102cc
Yellow	160cc

Transfer times can be effectively speeded up by having the transfer board mounted on a rigid "duck board" in a sink in which warm water can flow. If the transfer surface can be maintained at about 90 F. transfer times will be as follows: cyan 2, magenta 3, yellow  $1\frac{1}{2}$ , black 2 minutes. During transfer the matrix is covered with a damp towel which has been immersed in a tray of  $1\frac{1}{2}$  per cent acetic acid solution at 90 F. The towel will hold the edges of the matrix film in contact with the transfer paper, and the  $1\frac{1}{2}$  per cent acetic acid in the towel will prevent bleeding of dyes which might result from solution creeping between the matrix and the paper.

After transferring the "F" surface paper, the print is dried on a glossy drum dryer, or, if on "A" or "G" paper, the prints are rolled between dry blotters and hung up to dry. If a production run of matt surfaced prints is made, racks of frames covered with plastic window screening will be found useful.



Fig. 10. Use of soft rubber hose covered at the end with eight layers of cheese cloth for hot water rinsing the matrix films.





Fig. 11. Rocking table and replenishing buretts for dyeing the matrices.

On a single sheet of Dye Transfer Paper there are two pages of illustrations and each page might have as many as five illustrations. That is, 10 transfers have been accomplished in a single transfer operation. With planning in the layout, punching and exposing stages, the top and bottom edges of the pages can be positioned so that they can be trimmed at one cut of the trimmer. One inch is allowed at the left side for binding if the pages are to be bound with a printed text.

## SUMMARY

While the technique involved in the production of Simultaneous Multiple Dye Transfer Printing may seem involved and perhaps arduous, it has its place among methods of reproducing color transparencies in print form. The advantages of resolving fine detail, continuous tone and extended contrast range make it especially desirable for certain classes of transparencies, notably biological illustrations.

In practice, the actual production of these Multiple Dye Transfer prints did not seem as involved as this paper might tend to indicate. Some phases of this technique, particularly the method of diffusing masks and meter standardization, can be applied to ordinary Dye Transfer Printing.

At the expense of length, details have been described rather thoroughly so that the technique can be dupli-

cated by others. It is believed that any careful color photographer, versed in masking, separation and Dye Transfer theory and practice, can produce Simultaneous Multiple Dye Transfer Color Prints.

## Acknowledgments

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3. Eastman Kodak Company, Color Separation and Masking, 1951.
4. Eastman Kodak Company, Kodak Dye Transfer Process, 1951.

Fig. 12. Representative Record Sheets showing data on some of the illustrations made in this laboratory.

## ABSTRACT

Many scientific, educational and commercial organizations have need for a limited run of full color continuous tone print reproductions of color transparencies. This paper describes a system of reproducing several relatively small color prints simultaneously.

The advantages of continuous tone and extended contrast range make the Eastman Kodak Dye Transfer process especially desirable for the resolution of fine detail essential in photomicrography. The limitation of single illustration transfer has been a handicap to its general use as a method of reproducing prints in quantity. This limitation has been partially overcome and this paper covers in detail the production problems and their solution.

A novel method of diffusion of the highlight and principal masks is described as well as a consideration of color separation negative contrast range requirements of a wide variety of original subject matter. These items have applications to individual as well as to multiple Dye Transfer operations.

A novel system of registering sets of separation negatives and positioning them during exposure of the matrix film is covered in detail and illustrated. A method of adding arrows, lettering, and figure numbers to Dye Transfer prints is also described.

# FLUORESCENCE IN THE PHOTOGRAPHIC EMULSION

JOSEPH S. FRIEDMAN AND LESTER HORWITZ\*

## ABSTRACT

The fluorescence of pure silver halides and of photographic emulsions has heretofore been detected only at exceedingly low temperatures. A method has been evolved for measuring the fluorescence emission of emulsions at normal temperatures. This is accomplished by irradiating an emulsion with blue light and recording any emitted green or red fluorescent light on a panchromatic receiver. It has been established that emulsion additives influence fluorescence emission considerably. Particularly is this true for sensitizing dyes, which have been studied in some detail. With some dyes, the total fluorescence measured was more than the simple sum of the fluorescence due to the dye and to the emulsion separately. Other dyes showed a reverse or quenching effect. In some cases, the fluorescence of an emulsion could be quenched by pre-exposing the emulsion through blue or yellow filters; the quenching being somewhat dependent on the color of the pre-exposing light. Maximum fluorescence and maximum quenching occurs at constant dye concentrations for a given emulsion. These maxima are also related to maximum photographic speeds in the natural and induced ranges.

THE absorption of light by a silver halide grain in a photographic emulsion initiates a chain of events which under favorable conditions culminates in the formation of a latent image. As a result of this initial act, according to Gurney and Mott,<sup>1</sup> an electron in the system is raised into the conductivity level, where it is free to wander until trapped at some grain imperfection. This is an electronic process and is independent of temperature. The trapped electron constitutes a negatively charged point which attracts a positively charged interstitial silver ion. Upon union, the charges become neutralized and a silver atom is formed. When a sufficiently large number of silver atoms are generated at one point the grain becomes developable, i.e., a latent image is formed. The last step involves ionic migration and consequently has a high temperature coefficient. Any interference with either electronic or ionic migration will affect adversely the efficiency of latent image formation. From this it may be inferred that the efficiency of latent image formation drops off as the temperature falls, a fact verified by the experiments of Berg and Mendelsohn<sup>2</sup> Webb and Evans<sup>3</sup> and Meidinger.<sup>4</sup>

With each step in this series of events interchanges of energy take place. Energy is absorbed when an electron is raised into a conductivity level. Energy is required for the creation of interstitial ions and in their migration to the trapped electron under the influence of electronic charges. Since this involves the motion of an electrical charge, it should be accompanied by radiation. Energy is released when the interstitial ion unites with the trapped electron to form a silver atom. Each of the above are separate acts. Therefore, it should be possible to design experiments to detect and measure the energy exchanges. In some cases, when energy is given up, the released energy may be in the form of radiation capable of being recorded photographically.

Since the efficiency of latent image formation at low temperatures is not great, it was reasoned that the absorbed energy not utilized for latent image formation, may be re-emitted as fluorescence. At low temperatures other dissipative processes, such as vibrations and rotations, are minimal, enhancing the chances for fluorescent emission. This was demonstrated by a number of

people.<sup>5, 6, 7</sup> These researches disclosed that silver halides in the pure state, in mixtures, and when dispersed in gelatin, emitted fluorescent light when excited by light which they absorbed. The emission lay in the green and red portions of the visible range, just to the long wave length side of the absorption bands of the various silver halides. It had a very high temperature dependence, the emission being very strong at 70 K but no longer observable above 200 K. The dye sensitized emulsion behaved no differently from the unsensitized emulsion of otherwise identical composition. The same was true for other emulsion additives such as desensitizing agents, silver sulfide, silver-gelatin complexes, etc.<sup>7</sup>

These studies had at least two things in common. All used ultraviolet radiation to excite the test materials. All made their observations at temperatures below 200 K. This excluded the second step involved in latent image formation. Meidinger reported that the quantum efficiency of the fluorescing act approached unity.<sup>5</sup> This indicates that the trapped electron does not remain indefinitely in an excited state, but drops to its ground state with a concurrent discharge of the excess energy in the form of fluorescent light. It can also be inferred that the energy involved is that which under more favorable conditions would be used for latent image formation.

In this work the fluorescence of the photographic system at room temperatures was studied. The exciting light was the blue transmitted by a Wratten #49B filter. The fluorescent light emitted by the test material was recorded upon a panchromatic film after filtration removed any exciting light that was transmitted by the test materials.

## Experimental and Evaluation Procedure

In every experiment, four test materials were exposed to blue light simultaneously with an optical step wedge having densities ranging from 2.00 to 5.00. The emergent light was filtered to remove any blue that may have been passed, and recorded upon a panchromatic film. This filtration was not used for the light transmitted by the step wedge. The density of the image of the wedge served as an index whereby the intensities of the emergent light could be determined relative to that of the incident light. (Note illustration opposite).

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The Wratten #49B filter<sup>8</sup> has a maximum transmission at 450 m $\mu$ , and a transmission limit at 500 m $\mu$ . The Wratten #16 filter starts its transmission at 510. For a normal exposure, therefore, the two are mutually exclusive. Exposures were adjusted so that the intensity of the light transmitted by the two filters in superposition, was recorded as a point just above the fog level on the characteristic H&D curve of the recording film.

In each experiment test material #1 was film base coated with a layer of plain gelatin. This served to measure the intensity of the light transmitted by the two filters in superposition. Test material #2 was unsensitized photographic emulsion coated upon film base. Test material #3 was film base coated with gelatin that contained an emulsion additive (e.g., sensitizing dye) in varying concentrations. Test material #4 was the same emulsion as used in test material #2 containing, in addition, emulsion additives in the same concentrations present in test material #3. All coatings were 5  $\mu$  thick. The test materials were always interposed between the two filters with the blue facing the exposing light. The recording material was Ansco Triple S Pan Film. It was developed for 10 minutes in A-47 at 20 C.

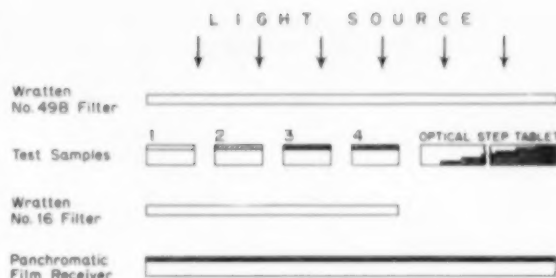
If the density obtained in the recording film for any of the test materials exceeded that obtained for test material #1, those materials exhibited fluorescence. The intensity of the fluorescence, relative to that of the exposing light, was determined by the methods of photographic densitometry. The densities in the recording material formed by exposure through the optical step wedge were plotted against the densities (log exposure values) of the steps in the wedge. This constituted the characteristic H&D curve for the recording film. The log exposure value for each test material was determined from this curve and represents the negative of the logarithm of the ratio of the intensity of the emergent light to that of the incident. A value of 4.00 means that the intensity of the emergent light was  $10^{-4.00}$  or one ten-thousandth that of the incident light. It was convenient to relate all findings to that of a reference point. This was accomplished by subtracting all log exposure values from that of test material #1, which served as the reference point and was gelatin coated film base. In essence, this was the same as arbitrarily choosing this as the zero point in the log exposure values scale. Since the scale is logarithmic in character, it was equivalent to assigning a relative value of 1.00 (anti-log of 0.00) to the intensity of light that was transmitted by the Wratten #49B and #16 filters in superposition.

## Experimental Results

### (A) The Fluorescence of Unsensitized Photographic Emulsions

Emulsions ranging in sensitivity from a Lippmann to a Cine Negative were tested. The results are given in Table I.

The values in the last column are the anti-logarithms of those in the second column. All the emulsions tested showed a small but definite fluorescence. The actual intensity is, however, 10 to 15 times that recorded. First, only that portion of the fluorescence was recorded which was directed toward the recording material, but



as much fluorescence was directed away from this material as was toward it; hence, at least a factor of two is involved here. Second, only that portion of the emission was recorded which escaped loss by scatter. A piece of test material #2 (unsensitized emulsion) when measured with red light in a color densitometer, gave a reading of 0.90. Since neither silver halides, gelatin nor film base have any appreciable absorption in this region, this can be taken as a measure of the loss of light by scatter; a factor of 8 (anti-logarithm of 0.90) is involved. Thus, the actual fluorescent intensity may be sixteen times that recorded.

Table I

FLUORESCENCE OF SOME NATIVE PHOTOGRAPHIC EMULSIONS (NO ADDITIVES)

Test Material	Log Exposure Value	Relative Intensity of Fluorescence
Test Material #1	0.00	1.00
Lippmann	0.12	1.32
Paper	0.05	1.12
Positive	0.11	1.29
Negative	0.10	1.26

### (B) The Fluorescence of Dye Sensitized Emulsions.

#### I. Positive Emulsion

##### (a) A Pseudocyanine Dye (Dye A).

This dye was one that exhibits J-band sensitization. The results are tabulated in Tables II and III. Here, only the relative intensities of the emitted fluorescence is given. The numbers represent the anti-logarithms of the corresponding log exposure values.

Table II

FLUORESCENCE OF EMULSION CONTAINING DYE A

Conc. Dye mgs./kg. Emulsion	Test Materials			
	#1 Gelatin Coated Base	#2 Unsensitized Emulsion	#3 Dyed Gelatin	#4 Dyed Emulsion
10	1.00	1.86	1.23	3.24
20	1.00	2.00	1.32	4.57
40	1.00	2.00	1.41	6.46
80	1.00	2.00	1.55	7.94
160	1.00	2.00	1.66	5.75

Let the assumption be made that each entity comprising a dye sensitized emulsion acts independently. Experiment has shown that neither film base nor plain gelatin fluoresce when excited by blue light. Then the relative intensity of the fluorescence from a dye sensitized

emulsion should be equal to the sum of the intensities from dyed gelatin (test material #3) and unsensitized emulsion (test material #2). In Table III is given a comparison of this sum with the experimentally determined value.

**Table III**

FLUORESCENCE OF DYED EMULSION (DYE A) COMPARED TO THAT OF SUM OF FLUORESCENCE OF EMULSION AND DYE

Conc. Dye mgs./kg. Emulsion	Unsen- sitized Emul. #2	Dyed Gelatin #3	Sum of #2 & #3	Experi- mental Value	Difference
10	1.86	1.23	3.09	3.24	+0.15
20	2.00	1.32	3.32	4.57	+1.25
40	2.00	1.41	3.41	6.46	+3.05
80	2.00	1.55	3.55	7.94	+4.39
160	2.00	1.66	3.66	5.75	+2.09

An examination of the values in the last column in both Tables II and III shows that a maximum fluorescence and a maximum superadditivity effect is obtained at a concentration of 80 milligrams of dye per kilogram of wet emulsion. Sensitometric data for these coatings indicate that at this concentration of dye, the sensitivity is at a maximum both for yellow light (induced range) as well as for blue light exposures.

(b) An Unsymmetrical Carbocyanine, (Dye B).

This dye was one that does not show J-band sensitization. The results are given in Tables IV and V.

**Table IV**

FLUORESCENCE OF EMULSION CONTAINING DYE B

Conc. Dye mgs./kg. Emulsion	#1	Test Materials #2	#3	#4
10	1.00	4.00	2.45	3.89
20	1.00	4.00	3.02	8.51
40	1.00	3.71	5.13	14.13
80	1.00	3.71	7.24	23.44
160	1.00	3.63	12.88	23.44

**Table V**

FLUORESCENCE OF DYED EMULSION (DYE B) COMPARED TO THAT OF SUM OF FLUORESCENCE OF EMULSION AND DYE

Conc. Dye mgs./kg. Emulsion	Unsen- sitized Emulsion #2	Dyed Gelatin #3	Sum of #2 & #3	Experi- mental Value	Difference
10	4.00	2.45	6.45	3.89	- 2.56
20	4.00	3.02	7.02	8.51	+ 1.49
40	3.71	5.13	8.84	14.13	+ 5.31
80	3.71	7.24	10.95	23.44	+12.49
160	3.63	12.88	16.51	23.44	+ 6.93

Again the maximum fluorescence and superadditivity occurs at a concentration of 80 milligrams of dye per kilo of wet emulsion, and sensitometric data indicates a maximum blue and yellow sensitivity for this concentration of dye.

The dyes A and B above form a class with a common pattern. Emulsions sensitized with them exhibit a

superadditive fluorescence. They emit light which is greater than the simple sum of the fluorescence of the dye and the native emulsion separately. The superadditivity reaches a maximum at the same concentration of dye as does the photographic sensitivity of the dyed emulsion. In the Tables below (VI to XI) are listed the values for another class of dyes.

(c) A Symmetrical Thiocarbocyanine (Dye C)

**Table VI**

FLUORESCENCE OF EMULSION CONTAINING DYE C

Conc. of Dye mgs./kg. Emulsion	Relative Intensities of Fluorescence of Test Materials #1	#2	#3	#4
10	1.00	1.62	1.28	1.86
20	1.00	2.04	1.74	2.24
40	1.00	1.74	1.55	2.04
80	1.00	1.74	2.00	1.70
160	1.00	1.74	1.74	1.74

**Table VII**

FLUORESCENCE OF DYED EMULSION (DYE C) COMPARED TO THAT OF SUM OF FLUORESCENCE OF EMULSION AND DYE

Conc. of Dye mgs./kg. Emulsion	Emulsion #2	Dye #3	Sum of #2 & #3	Experi- mental Value #4	Difference
10	1.62	1.28	2.90	1.86	-1.04
20	2.64	1.74	3.78	2.24	-1.54
40	1.74	1.55	3.29	2.04	-1.25
80	1.74	2.00	3.74	1.70	-2.04
160	1.74	1.74	3.48	1.74	1.74

(d) A Symmetrical Meso-substituted Thiocarbocyanine (Dye D)

**Table VIII**

FLUORESCENCE OF EMULSION CONTAINING DYE D

Conc. Dye mgs./kg. Emulsion	Relative Intensities of Fluorescence of Test Materials #1	#2	#3	#4
10	1.00	2.34	1.59	2.04
20	1.00	2.04	1.38	1.74
40	1.00	2.00	1.51	1.32
80	1.00	2.00	1.55	0.77
160	1.00	2.24	1.78	1.78

**Table IX**

FLUORESCENCE OF DYED EMULSION (DYE D) COMPARED TO THAT OF SUM OF FLUORESCENCE OF EMULSION AND DYE

Conc. Dye mgs./kg. Emulsion	Emulsion #2	Dye #3	Sum of #2 & #3	Experi- mental Value #4	Difference
10	2.34	1.59	3.93	2.04	-1.89
20	2.04	1.38	3.42	1.74	-1.68
40	2.00	1.51	3.51	1.32	-2.19
80	2.00	1.55	3.55	0.77	-2.78
160	2.24	1.78	4.02	1.78	-2.24



(c) A Symmetrical Oxacarbocyanine (Dye E).

**Table X**

FLUORESCENCE OF EMULSION CONTAINING DYE E

Conc. Dye mgs./kg. Emulsion	Relative Intensities of Fluorescence of Test Materials	#1	#2	#3	#4
10	1.00	2.82	2.88	3.24	
20	1.00	2.24	3.09	2.69	
40	1.00	2.46	6.31	4.47	
80	1.00	2.46	8.51	4.90	
160	1.00	2.46	14.45	12.02	

**Table XI**

FLUORESCENCE OF DYED EMULSION (DYE E) COMPARED TO THAT OF SUM OF FLUORESCENCE OF EMULSION AND DYE

Conc. Dye mgs./kg. Emulsion	#2	Dye #3	Sum of #2 & #3	Experi- mental	Difference
10	2.82	2.88	5.70	3.24	-2.46
20	2.24	3.09	5.33	2.69	-2.64
40	2.46	6.31	8.77	4.47	-4.30
80	2.46	8.51	10.97	4.90	-6.07
160	2.46	14.45	16.91	12.02	-4.89

The last three dyes (Dyes C, D, and E) form a class with a pattern that is the exact opposite of that of the previous group (Dyes A & B). Here, there is indicated a quenching of fluorescence. The dyed emulsion emits less light than the simple sum of the fluorescence of the dye and the native emulsion separately. But the two classes have one property in common. Maximum super-additivity or quenching is at a concentration of 80 milligrams of dye per kilo of emulsion. This value is evidently a constant for the emulsion. It is at this concentration of dye that the induced sensitivity of the emulsion is at a maximum. It is also the concentration at which the blue sensitivity just begins to fall off, where the desensitizing action of the sensitizing dye begins to be felt. It would be expected that more accurate determinations of the concentration necessary for maximum effect will show slight deviations from dye to dye, since the different dye molecules have different chain lengths; hence, cover different areas.

The character of the fluorescence was a property of the dye. If a given dye produced a quenching or a super-additive effect in one emulsion it produced a similar effect in all emulsions tested. The results in each case were qualitatively the same, though quantitatively different. From this point of view, sensitizing dyes could be grouped into either quenching or superadditive types.

## II. Emulsions with Varying Grain Size

The maximum fluorescence obtained in the case of a positive emulsion apparently coincided with that dye concentration needed for a coverage of grain surface. Each type of emulsion had a characteristic value for the dye concentration needed to produce maximum fluorescence. A series of other emulsions were tested, differing in grain size from almost colloidal state to approximately one micron. The values obtained are shown in Tables XII to XIV. All the emulsions below were sensitized with Dye A.

(a) Lippmann Emulsion. The grains are practically colloiddally dispersed.

**Table XII**

FLUORESCENCE OF LIPPMAN-TYPE EMULSION

Conc. Dye mgs./kg. Emulsion	0	15	30	60	125	250	500	1000
Relative Fluorescence	1.51	3.16	4.90	7.94	8.91	13.14	9.12	2.95

The maximum is at a dye concentration of 250 mgs. per kg. of wet emulsion.

(b) Negative Emulsion. These contain grains that are quite coarse.

**Table XIII**

FLUORESCENCE OF NEGATIVE-TYPE EMULSION

Conc. Dye A mgs./kg. Emulsion	0	10	20	40	80
Relative Fluorescence	1.82	2.57	3.80	4.37	3.98

The maximum is at a dye concentration of 40 mgs. per kg. of wet emulsion.

(c) Paper Emulsion.

**Table XIV**

FLUORESCENCE OF PAPER-TYPE EMULSION

Conc. Dye A mgs./kg. Emulsion	0	10	20	40	80	160	320
Relative Fluorescence	1.12	1.86	2.82	2.82	4.68	5.62	1.66

The maximum here is at a dye concentration of 160 mgs. per kg. of wet emulsion.

It is evident that each emulsion exhibited a characteristic value for the concentration of sensitizing dye giving maximum fluorescence. This was also the concentration needed to produce maximum induced sensitivity and minimum loss of native sensitivity.

## III. Emulsions with Varying Iodide Content.

A series of emulsions, sensitized by Dye A, were prepared that differed in the amount of silver iodide they contained. The distribution of grain sizes was approximately alike. The results are tabulated in Table XV.

**Table XV**

EFFECT OF IODIDE CONTENT ON FLUORESCENCE

Mol. % Iodide	Fluorescence at Different Dye Conc. (mgs./kg. Emulsion)				
	0 mgs.	20	40	80	160
A 0.00	1.20	5.89	9.33	8.91	6.17
B 1.00	1.41	5.62	10.72	9.55	4.90
C 2.00	1.38	6.92	7.08	6.76	6.31
D 3.00	1.38	5.01	8.51	7.94	5.25
E 4.00	1.38	5.50	8.71	7.76	4.90
F 5.00	1.20	5.37	6.76	5.50	4.17

In all cases the maximum effect is at a dye concentration of 40 milligrams per kilogram of emulsion. On the average, there appears to be a slightly higher effect when the iodide content is approximately 1 mole percent. With higher iodide content the fluorescence appears to diminish. The sensitivities of the emulsions appear to vary in the same manner, both in the native and in the induced ranges.

(C) *The Effect of Exposure on Fluorescence.*

The exposures used in these experiments were sufficient to yield H and D curves for the recording film whose straight line portions extended to a point that corresponded to a density of 4.00 in the optical step wedge. This was approximately 100 times the normal exposure for Triple S Pan. However, it was only slightly on the over exposure side for the test materials. When the exposure was increased several times beyond this, some interesting effects were noted in the case of the positive emulsion sensitized with Dye A. The emitted light did not record the corresponding increases. This is shown in Table XVI, for the case of the positive emulsion sensitized with 80 milligrams of Dye A per kilogram of wet emulsion.

Table XVI

CHANGES IN FLUORESCENCE OF DYE A WITH CHANGING EXPOSURE TIME

Time of Exposure in Seconds	8	15	30	60	120
Relative Intensity of Fluorescence	8.91	10.96	8.71	6.17	4.17

The noted decrease in fluorescence cannot be explained by the formation of photolytic silver within the test material. The density of a strip of test material given many times the exposures used increased in value only 0.15 or one-half stop. From this, it is apparent that the ability of the test material to emit fluorescence was a function of exposure. This was further tested by giving strips of the sensitized positive emulsion pre-exposures to blue light. The pre-exposed strips together with an unexposed one, were then tested for fluorescence. The results are tabulated in Table XVII.

Table XVII

CHANGES IN FLUORESCENCE OF DYE A WITH DIFFERENT PRE-EXPOSURES TO BLUE LIGHT (WRATTEN NO. 49B)

Time of Pre-Exposure in Seconds	Fresh	5	10	20	40	80
Relative Fluorescence	7.24	6.46	6.17	4.68	2.95	2.69

Since the ability of the test material to fluoresce appeared to be affected by the presence of a latent image, the manner of formation of the latent image should be immaterial. According to present concepts, latent images formed by blue or yellow light exposures are indistinguishable. Quenching experiments were repeated using yellow light for the pre-exposure. Fluorescence was then measured in the usual way. The results are given in Table XVIII.

Table XVIII

CHANGES IN FLUORESCENCE OF DYE A WITH DIFFERENT PRE-EXPOSURES TO YELLOW LIGHT (WRATTEN NO. 16)

Time of Pre-Exposure in Seconds	Fresh	5	10	20	40	80
Relative Fluorescence	7.59	7.76	7.94	7.59	6.92	5.37

Sensitometric tests indicated that the emulsion tested gave somewhat greater densities when exposed through a Wratten #16 filter than when exposed for the same length of time through a Wratten #49B filter. Hence, the pre-exposure used for the latter experiment was somewhat greater than that for the first. Only when the pre-exposure to yellow was extended several more stops did the relative fluorescence fall to a value comparable to that obtained with an 80 second blue light pre-exposure.

In this instance, at least, it appears as if differences might exist in the properties of latent images formed by blue or yellow light.

This dependence of fluorescence upon exposure was utilized to prepare a direct dupe. A strip of test material (positive emulsion sensitized with 80 milligrams of Dye A) was exposed with blue light under a negative for 80 seconds. The negative was removed and the test material placed over a Wratten #16 filter. Under the filter was placed a strip of Triple S Pan film. The pack was then given an overall exposure to blue light, with the test material facing the light. The Triple S Pan film was developed in A-47 for ten minutes. A duplicate of the original negative was thus obtained.

As a result of the exposure under the negative, there was formed within the test material a positive pattern consisting of areas capable of emitting fluorescence. Upon the subsequent exposure, the emission of the fluorescent areas was recorded upon Triple S Pan film. Where the first exposure was heavy, the test material lost its ability to fluoresce, and a corresponding low density was obtained in the recording material. Where the first exposure was low, the test material retained its ability to fluoresce and a relatively heavy deposit was obtained in the recording material. The fluorescence was emitted in all directions so that the image obtained was diffuse. The separation of the thickness of a Wratten #16 filter between the source of the light forming the image, and the receiver, accentuated the poor definition markedly. It might be expected that fluorescence within a panchromatic emulsion caused by excitation by blue or green light may play some role in the image definition obtained in that material.

## Summary and Conclusions

The silver halide grain of a photographic emulsion exhibits a small but measurable fluorescence when excited by blue light at room temperature. The intensity of emission is affected considerably by the addition of sensitizing dyes. These can be classified into two groups. The first consists of those dyes which show a greater emission than would be expected were dye and emulsion to act independently. The second consists of those dyes which show a quenching effect, in which the

emission is smaller than would be expected were action/independent. The intensity of emission from a positive emulsion sensitized with Dye A decreases if there is already present within that emulsion, a latent image formed by a blue light exposure. The reduction in emission intensity is negligible in the case where the pre-exposed latent image was made by a photographically equivalent yellow light exposure. If, however, this be increased a number of stops, the emission due to a subsequent blue exposure, becomes appreciably reduced. The reduction in emission intensity by blue or yellow light is appreciably greater than could be accounted for by the formation of photolytic silver. The energy involved in the fluorescence is probably not that which would otherwise be used for latent image formation. Its intensity is a small fraction of that involved in that operation. The maximum effects exhibited by dye sensitized emulsions (superadditivity or quenching)

appear to coincide with maximum photographic activity. For that reason, the energy may be that which is involved in the chain of events which follow the initial absorption of light by a silver halide grain in a photographic emulsion.

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# PHOTOGRAPHIC EVIDENCE AND THE COMMERCIAL PHOTOGRAPHER

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IN THE process of supplying the needs of the legal profession in quite a number of matters relating to the use of photography for the production of evidence, there has inevitably been accumulated an orderly method of arriving at the required product. It has been necessary on occasion to employ other photographers to assist in this rather specialized field. Because it was difficult to obtain the required performance from these occasional helpers, a brief set of suggestions was formulated for their guidance. The idea has been expanded to include a regular text for professional photographers who may be called upon to perform this type of work.

This effort does not seek to minimize the excellence of the texts now in use touching this field. Unfortunately, they are generally slanted toward the use of photography in criminalistics, or else to the needs of the police specialist and his peculiar problems. The typical legal text is unattractive to the usual professional photographer for it is large in size, exhaustive in treatment, and slanted toward the interests of the lawyer more than the photographer.

## The Forensic Photographer

Fiction, motion pictures and television, all combine to give a false impression of a forensic photographer. That excellently done TV show starring Jack Webb as Sgt. Friday, one night showed what purported to be a police photographer taking photographs of a room to record the evidence. Unfortunately, Jack Webb's passion for correctness failed in that detail and the tele-

vision audience had the usual portrayal of a sort of slaphappy operator with a Graphic who hurried in, held the camera to his eye, popped a flashlamp, and was off.

If a forensic photographer carried out an assignment in an important legal matter in that slipshod, and quite uncharacteristic manner, that would probably be his last opportunity in the field. Fortunately, there exists in this profession a standard of proficiency which forbids such poor workmanship and sloppy appearance.

Practically speaking, *evidence* is something that you can see, hear, smell, taste or feel. Webster's Unabridged Dictionary, under the particularization of *Law*, gives, in part: *evidence*, "That which is legally submitted to a competent tribunal as a means of ascertaining the truth of any alleged matter of fact under investigation before it, etc."

Even the photographer who is a thoroughly good workman may have a real problem facing him when he is called by a lawyer to make a photographic record of details vital to the prosecution or defense of a suit at law. The first and greatest difficulty arises from the nature of the desired end-product. The lawyer wants the photographs so that he may bring them to court, introduce them as *evidence*, have them accepted, and by their use prove to the court that a certain physical situation (the subject of the photographs) did exist at a specified time and place. He further needs to be able to prove to the court that the photographs are a fair and accurate representation of that physical situation as it existed at the time the photographs were taken. And last, the photographer must take every picture with the full realization that he may be called into Court for veri-

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fication and that this appearance may occur any time in the next five years.

### A Typical Case

Early in January of 1951, an assignment was received from the local adjustor for a large insurance company. In this case the company had insured a manufacturer against losses arising from claims of faulty workmanship or manufacture of their products. On a large construction job, towers had been built as preparatory facility to massive construction at a considerable height. Materials were handled from these towers. Two men had been killed during the project when a sling of heavy girders suddenly fell, and it had then been alleged that this accident was due to a faulty sheave, manufactured by the company insured. A suit was pressed for \$100,000 for wrongful death.

The problem at hand was photography of the large snatch block involved in the claim, and of its integral parts, particularly that part presumed responsible for the mishap. There was a considerable undertaking on the part of the photographer in this case for there were exposed 19 black and white films, two plates, and three shots on Kodachrome transparencies, all made in the studio. Additionally, there was the original charge for a trip to the office of attorney for plaintiff in the matter, and another trip to the manufacturer to check final detail, proper nomenclature for the component parts of the snatch block, the making of sets of prints for plaintiff's lawyer, for the defendant, for defendant's insurance company, and finally for the law firm representing the insurance company.

Figure one shows two photographs made of the entire snatch block. Visible in the quartering view on the left are the manufacturer's imprint of his type number, some white lettering dating to the user company (these necessary to prove the derivation of the equipment), and under a piece of scotch tape, on the leading edge of the shell, the legend, "J. R. Banks 7-14-50." The photographs were taken with a Deardorff camera, Eastman 8 inch lens, on 4 X 5 film. The lighting in front came from two Baby KefLites. A translucent screen background was illuminated from behind by a bare photo-flood lamp. Swings were used to focus the major flat surface at maximum detail and the lens was stopped

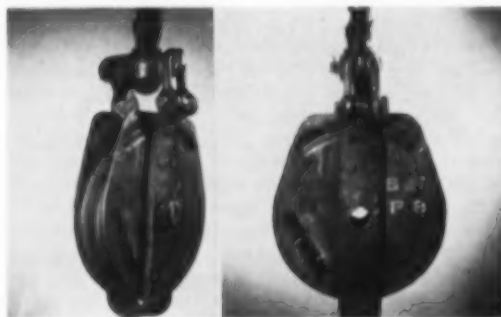


Fig. 1. Two views of a drop-link snatch block described in a law suit as faulty equipment and alleged to have caused a wrongful death. In the right hand view the center-pin and sheave have been removed.

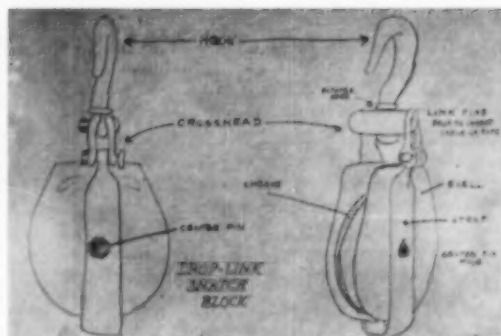


Fig. 2. Photographer's rough pencil sketch made from the manufacturer's explanation of the proper nomenclature for parts of the snatch block and useful later in case of a court appearance in connection with the photography.

down to extend the range of sharpness over the entire body. The front view on the right in Figure one shows the snatch block with center pin and sheave removed.

In addition, a plan sketch of the block in two positions was made, from the manufacturer's instructions, for the photographer's instruction and guidance. This is illustrated in Figure two as an example of the importance of details in doing a workmanlike job. By its use the component parts of the device could be identified at a later date and it could be used to refresh the photographer's memory in the event he had to go to a courtroom and testify concerning the photography.

When the photographs in Figure one were made, a written notation was made describing the photographs for future reference. One read: "510130-005 A photograph taken about 11:35 PM, Jan. 30, 1951 of a drop-link snatch block labeled, "J. R. Banks 7-14-50." The block hangs free, turned at an angle of about 30° to lens axis, center-pin and sheave are in place, with nut on finger tight, and sheave turned until it was at greatest apparent displacement from concentricity with shell."

The center-pin was going to be one of the chief witnesses in this case, but it had to be approached by degrees. Before taking pictures of it, every detail of the snatch block was photographed with maximum effort to retain an effective perspective, and to make the pictures sharp in detail. Only then was the center-pin photographed. Figure 3 shows one view of it and its nut, with the pin (or bolt) turned so that it showed the minimum cross section and therefore the maximum effect of wear. Part of the background, to help indicate size, was a black-on-white draftsman's scale. Another view, showing a slanting view of the worn area, was taken on a glass plate illuminated below to avoid having to block out.

Figure four is a close-up photograph of the strap area where the center-pin fitted in the side of the snatch block. Taken with view camera and a short focal length lens (Wollensak 3 3/8 inch Wide Angle Optar) at a distance of five inches from the block, this picture was enlarged to 16 X 20 and mounted for easy handling. Presented in that manner it showed graphically the eccentricity and irregularities of the holes in the shell where the center pin fitted.



## The Plaintiff's Case

The plaintiff's attorney had thought well enough of the possibility of recovery in this matter to spend quite a bit of his own funds in taking depositions from persons who might have been witnesses or had some information pertinent to the case. He had travelled some thousands of miles, and had filed his suit in U. S. Federal District Court. He was not in business for his health but counted on getting his expenses back, plus a nice percentage of whatever the court might finally award the heirs and devisees of the dead men. Subsequent acquaintance bears out that he is a canny gentleman. He had undoubtedly consulted with some experts in the field of heavy equipment and felt that his clients had a worthwhile suit. It seemed apparent when he displayed the principal piece of evidence that he felt rather proud of it. He asked for assurance by defense counsel of the photographer's reliability and trustworthiness, finally formalized by a carefully worded, signed receipt, before he permitted the block to be taken from his office.

However, within a few months after these pictures were in the hands of the parties to the case, a settlement was had with the plaintiffs for about three thousand dollars. What had happened in the meantime? Nothing had happened except that, by the aid of photographs,



Fig. 3. The center-pin and nut photographed at the minimum cross section to illustrate the extent of wear and deformation.

the defendant counsel had been able to shatter the whole theory of the plaintiff's counsel as to the probable blame in the matter. Instead of the presumption that the mishap had occurred because the manufacturer had supplied plaintiff's employer with a defective and improperly made snatch block, it had been revealed by photography that this important tool of the construction worker had been abused. It was the very exhibit that counsel for the plaintiff had guarded so carefully that proved his undoing. It carried all the scars and corrosion from a much abused life. Apparently it had been used over a considerable period with no lubrication; it bore deep rust spots. Experts in the field of heavy construction positively identified sure indications of such negligence in the use of the snatch block. This testimony made burden of proof on plaintiff-counsel extremely difficult. The settlement represented a fair allowance to counsel of the nuisance value of the suit in deference to his out of pocket expense.

What the photographer did in this matter was to

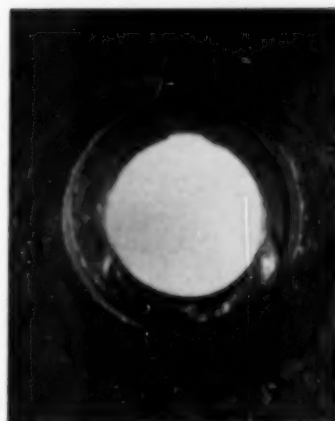


Fig. 4. Close-up photograph of area in the side of the snatch block where the half inch diameter center pin fitted.

listen carefully to defense counsel, and to the engineers representing his client, and then work to the best of his ability to give them just what they wanted. Color film was used, backed up with gray card, gray scale and process color chart, to show the real rust and corrosion. Lights were measured, moved and the cameras focussed and refocussed, to get the detail and sharpness required. The photographer tried, during the time spent to make these pictures, to identify himself intimately and completely with the problem in hand. He relied on his five senses to tell him what was there to be found, using the plan sketch of the snatch block to be certain the proper terminology was in clear descriptions, and making careful notes at every step.

Because the photographer who wants to specialize in photographic evidence has to strive for the highest ethical standards, it will be understood that the cases he works on are rather evenly divided between those for defendants and those for plaintiffs. The following is an example of the latter.

## More Photographic Evidence

In 1951 an out of town company had a number of men at work in a local manufacturing plant that made crankshafts. The specialists were installing and getting into effective production a device that would harden crankshafts by flame-treating followed by an oil quench. The flame was produced by a mixture of propane and oxygen, which not only can produce considerable heat, but which also can be an explosive mixture.

One morning when a tremendous explosion shook the town there must have been a number of the local people who guessed right away what had happened. The knowledge of the hazard connected with the explosive mixture had become well known. The guessers were right, for the specially constructed brittle shell of the building housing the heat treating equipment was scattered far and wide, and no one who had been in the building was left alive to tell what had happened.

There was plenty of direct evidence that an explosion had occurred. There was, however, nothing but indirect and circumstantial evidence to show how it had happened. Within an hour an insurance investigator had the local photographer on the scene. The investigator directed the views he wanted taken. Fortunately

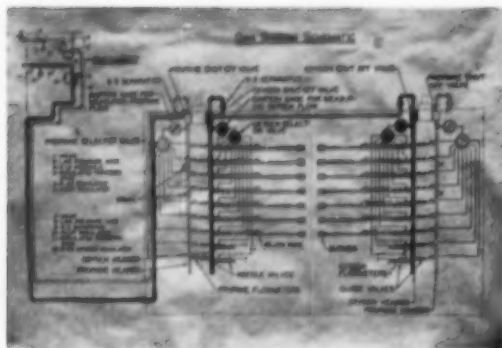


Fig. 5. Chart introduced in evidence by the defense in a lawsuit and photographed by the plaintiff in the courtroom during a recess while the trial was in progress. This photograph aided plaintiff later when the case went before the appellate court.

for the widow of one of those killed, this photographer was a local man, interested in the life of his community, and alert to business promotion. After the investigator left, one of the men from the local plant approached the photographer and told him there were some more things he ought to photograph, just for the record. This workman had found some valves, presumably uniform in use, but one of them was open, the other closed. The photographer obliged, for the local company was one of his regular accounts, and the local people were not only his neighbors but the main source of his bread and butter. He took a number of photographs that day, and later presented them, *with the negatives*, to the president of the local company. The company president promptly put both prints and negatives in a safety deposit box.

One of the men who was killed in the explosion worked for the local company. The State of Ohio has an Industrial Compensation System that provides for the widow and family of men hurt or killed at their work. The story might have ended right there, except that the widow of this man was led to consult an attorney on the question of liability by the installing company due to negligence on the part of their workmen. After a long period of investigation, her counsel discovered the "extra pictures" made the afternoon of the explosion. These pictures added a great deal to what had been deduced from the first set of pictures directed by the investigator. They told enough so that from the whole batch of photographs, and others which were added by various experts as the preparation for trial went its course, a comprehensive theory of inferences was evolved. These inferences seemed to point to error, to mistakes in basic design and errors in the judgment of the installing group and in their manipulation of the controls, valving and preparatory safety measures for machine operation.

Trial, brought in the Court of Common Pleas of Cuyahoga County, lasted nineteen days. Near the end of the trial, the defense brought into the courtroom a rather large exhibit on a white card, which showed the piping diagram of the crankshaft flame-hardening device. The paths of oxygen and of propane were shown by

yellow and green coloring of those pipes on the exhibit. Counsel for the plaintiff realized as the period went on that this diagram added a missing piece to the jigsaw puzzle they had been assembling. They felt sure, with so bitterly fought a case, that whoever won, the case would be appealed. And here was a new piece of the story that could help in their brief for the appeals court. The plaintiff's counsel telephoned from the bailiff's office for a photographer to be in the court room at the noon recess.

Responding to this urgent call, the photographer found plaintiff's attorneys waiting beside the defense's exhibit, the engineering drawing of a piping plan shown in Figure five with its colored designation of gas direction. A photograph was taken of this chart in a very ordinary manner using a synchronized flash near the camera, which was on a tripod. With Type B pan film in the holders, an X-1 filter was used over the lens to provide a nearly correct rendering in monochrome of this yellow, green, black color combination. The negative was printed on 16 X 20 double weight paper and delivered the next morning.

### The Value of One Picture

The photographer heard no more about the case until months later when he found out how very important just one picture can be. The case in Common Pleas Court wound up with the jury awarding the widow \$75,000. Appeal was immediately announced by the defense.

Plaintiff counsel went back to work. They had something to work with that they had not had before, for now they knew the theory of the flame-hardening machine. Because the photograph let them separate the propane and oxygen lines they entered this battle with new spirit. Their foresight and one effective photograph had equipped them with a new tool.

Judges Skeel, Hurd and Kovachy ordered a remittitur (reduction of the award) of \$15,000, so that this award now stands at \$60,000, but affirmed otherwise without opinion. Plaintiff counsel is now looking to the Supreme Court of the State of Ohio for certification of the result which may occur as this goes to press. Plaintiff counsel feels confident of the result, and declares that the use of photography was completely responsible for their success here. The photographs let them evolve a theory as to what happened, and since there were no survivors of the explosion, photographs were the principal witnesses. Finally, one particular last-minute photograph provided the last principal bit of missing information.

The evidential assignments which come to a forensic photographer present an amazing variety. This paper mentions only a small but characteristic segment of the field. Very little has been said about perspective considerations, and that problem alone is of enormous importance in presenting photographic evidence which seems to be correct in a manner that is easily understandable and believable.

It is a delightful experience to find the many experts in many fields who are ready to help us as we look for better answers to our problems. The lawyers and scientists have both been unsparing in their assistance to me in my work.

# A SIMPLIFIED FILM-PROCESSING PROCEDURE FOR THE TROPICS\*

M. D. Little

## ABSTRACT

A suitable processing procedure for temperatures up to and including 85 F involves use of the low-alkalinity highly salted developer, Kodak D-23, the sulfated acetic acid stop bath, SB-5, and the relatively odorless potassium alum hardening fixer, F-6.

This procedure minimizes emulsion swelling and fogging during development, avoids excessively rapid development rates, and imparts adequate hardening to the film so as to withstand washing at correspondingly high temperatures.

Tank development times at 85 F for an average gamma of 0.8 are from 6 to 7 minutes with most high-speed emulsions.

The developer is replenished with Kodak Replenisher D-25R, and the activity of the stop bath is maintained with 28% acetic acid added to a volume equivalent at one-half that of the D-23 carried into the stop bath.

In the tropics the photographer is constantly confronted with film-processing problems resulting from the relatively high prevailing temperatures and humidities of these regions. A review of the developers used throughout tropical areas indicated that Kodak Developer D-76 and Kodak Developer DK-50 are commonly employed, but it is well known that these do not offer the minimum degree of swelling and maximum freedom from fog so essential at temperatures predominantly in the 85 F range.

It is possible to obtain the desired characteristics by making additions to the original formulas of such developers or by using extra processing steps, but neither of these practices has been popular, owing to the added time and expense involved. Aside from these problems, there are also the disadvantages of the stop baths and fixers in common use.

Recent work at the Kodak Tropical Research Laboratory in Panama, R. P., has resulted in a simple, economical film-processing procedure adaptable for temperatures up to and including 85 F. The procedure minimizes emulsion swelling and fogging during development, reduces excessively rapid development rates, and produces adequate hardening of the film so as to withstand washing at correspondingly high temperatures.

Briefly, the system includes the low-alkalinity highly salted developer, Kodak D-23, a highly sulfated acetic acid stop bath—double strength (SB-5), and the moderately acid potassium alum hardening fixer, F-6. Formulas are given in Tables I, II, and III.

A group of Kodak film emulsions, including Super Panchro-Press Type B, Portrait Panchromatic, and Tri-X Panchromatic sheet films, Super-XX 35mm and Verichrome roll films, and Super-XX film pack have been investigated, using this processing system. Of these, only Tri-X Panchromatic is not commonly marketed in

tropical areas. Tank development times of 6 to 7 minutes at 85 F in D-23 are sufficient to give an average gamma of 0.8 with all the films listed except Super-XX 35mm for which 8 to 9 minutes are required. The intervals can be reduced by about 1 minute, if processing is carried out in a tray with somewhat greater agitation.

Tri-X Panchromatic is rather easily damaged during development at 85 F and, for this reason, should not be processed in these solutions. All other emulsions are handled without excessive softening or swelling during development, and reticulation rarely occurs under these conditions. The developed fog is negligible and the "speed-to-graininess ratio" approaches that of D-76 Developer. D-23 is almost entirely free from staining tendencies and its keeping life is excellent.

Developer D-23 has a relatively short life of from twenty to thirty No. 620-size rolls, or their equivalent, per gallon, but this may be increased to an excess of 100 rolls per gallon and constant activity maintained by replenishment with D-25R in the proportion of  $\frac{3}{4}$  ounce per roll processed. The formula simplicity of the developer-replenisher combination favors its use from both a cost and time-saving point of view.

Since the emulsion swelling is only slight during development, it is merely necessary to arrest development by immersing the film for one to three minutes in the non-swelling acetic acid bath, double strength SB-5. Although this does not permanently harden the film, like a chrome alum bath, it prevents it from swelling until it reaches the hardening fixing bath, and it is free from the objectionable scumming and poor keeping properties of chrome alum baths. The acetic acid-sulfate bath also offers the advantage that it may be readily revived by replenishing with acid. Over extensive processing periods, this practice of replenishment is profitable because essential salts are not discarded after each neutralization. The acidity is maintained with 28% acetic acid added in a volume equivalent to half the D-23 carried into the stop bath. In this way the normal life of 75 rolls per gallon is extendible to 300 rolls.

\*From the Tropical Research Laboratory, Panama, R. P., of the Kodak Research Laboratories, Rochester 4, N. Y. Presented at the Symposium on Photographic Processing preceding the PSA National Convention in Chicago, Illinois, 5 October, 1954. Received 27 September, 1954.

When considering a film fixer for tropical use, one must take into account the hot, humid, poorly ventilated darkrooms commonly encountered. The conventional potassium alum hardening fixers, such as Kodak Acid Fixer and Kodak F-5, evolve sufficient sulfur dioxide to cause serious irritation. Formula F-6, on the other hand, is relatively odorless. A fixing time of 10 to 15 minutes in this bath at 85 F, followed by a 30-minute wash, furnishes a well-hardened hypo-free negative.

Mr. H. T. Lewis, a photofinisher and portrait photographer of Cristobal, Panama Canal Zone, has recently made deep-tank processing trade tests of the procedure just outlined. The quality of his work is excellent as judged by the processed sensitometric and camera-exposed Verichrome films sent to him weekly by the Kodak Tropical Research Laboratory.

During processing no difficulties have been encountered, and it is the opinion of Mr. Lewis that the D-23-D-25R combination is superior in many respects to D-76-D-76R which he previously employed. Only a gradual increase in development time is necessary after many weeks of processing to maintain optimum photographic characteristics. However, somewhat more frequent replenishment is necessary than with D-76.

The stop bath and fixer present no problems, and the films, after 10 to 15 minutes' fixing and 30 minutes' or more washing at 85-87 F, are in excellent condition. Mr. Lewis's darkrooms are typically small, and the odorless quality of F-6, as compared to that of the F-5 previously used, is expressly appreciated.

Further trade tests are under way in the tropics to indicate more fully the acceptability of the processing cycle for photofinishing and general use.

**Table I**

RECOMMENDED DEVELOPER AND REPLENISHER FOR TROPICAL USE

	Kodak D-23	Kodak D-25R
Water, about 125 F (50 C)	750.0 cc.	750 cc.
Kodak Elon Developing Agent	7.5 grams	10 grams
Kodak Sodium Sulfite, desiccated	100.0 grams	100 grams
Kodak Balanced Alkali	...	20 grams
Cold water to make	1.0 liter	1 liter

**Table II**

TROPICAL STOP BATH

	Kodak SB-5 (Double Strength)
Water	500 cc.
Kodak Acetic Acid, 28%	64 cc.
Kodak Sodium Sulfate, desiccated	90 grams
Water to make	1 liter

**Table III**

TROPICAL FIXER

	Kodak F-6
Water, about 125 F (50 C)	600 cc.
Kodak Sodium Thiosulfate (Hypo)	240 grams
Kodak Sodium Sulfite, desiccated	15 grams
Kodak Acetic Acid, 28%	48 cc.
Kodak Balanced Alkali	15 grams
Kodak Potassium Alum	15 grams
Cold water to make	1 liter

## INTERNATIONAL SYMPOSIUM ON HIGH-SPEED PHOTOGRAPHY AND KINEMATOGRAPHY

P. Naslin\*

Nearly 200 members of the French Association of Motion Picture Engineers and Technicians (AFITEC) and more than 100 visitors from 18 countries attended the Second International Symposium in Paris, September 22 to 28, 1954. The First International Symposium on High-Speed Photography had been held in Washington, D. C. in October 1952 under the auspices of the SMPTE. This Second Symposium had been arranged by AFITEC with the cooperation of the British Kinematographic Society, the Deutsche Kinotechnische Gesellschaft, and the Samfundet Svenska Film Ingenjörer.

The proceedings comprised 5 lectures and 66 papers covering 10 half-day sessions. In addition there was an exhibition of some 30 instruments including nearly all the commercially available high-speed cameras. The Symposium illustrated the increasing world interest in the photographic investigation of rapid events in the most varied branches of science and technology, from ballistics to biology, in fields of metallurgy,

mechanical engineering, aeronautics, electricity, physics, chemistry, etc.

It was made clear that short exposure-times and high taking rates are not limited to the study of fast phenomena. The time of exposure must be made small also for decreasing object sizes, to prevent blur. The rather elementary remark that microscopic observation often leads to high taking rates is not always familiar to potential users and should be capable of opening new fields of application to high-speed techniques.

The technical papers dealt with the following general subjects: Flash sources, High-Speed Shutters, High-Speed Cameras, Lighting, Sensitive Layers, and Application of High-Speed Photographic Methods.

The complete Proceedings of the Symposium will be published by AFITEC and will be available at about 8 to 10 dollars, the price to be determined later and dependent somewhat on the number of orders received. Orders and inquiries should be addressed to the Organizing Secretary, Ing. Ppal. P. Naslin at the address shown below. Each paper will be printed in the language chosen by its author (French, English or German) and the summaries and figure captions will be printed in all three languages.

\* Organizing Secretary, 2e Congrès International de Photographie et Cinématographie Ultra-Rapides, Ingénieur Principal de l'Armement, Fort de Montrouge, ARCUEIL (Seine) Paris, France. Received 17 January, 1955.